SANDIA REPORT

Solution Synthesis and Processing of PZT Materials for Neutron Generator Applications

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Sandia National Laboratories

SOLUTION SYNTHESIS AND PROCESSING OF PZT MATERIALS FOR NEUTRON GENERATOR APPLICATIONS

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Abstract

A new solution synthesis route has been developed for the preparation of lead-based ferroelectric materials (patent filed). The process produces controlled stoichiometry precursor powders by non-aqueous precipitation. For a given ferroelectric material to be prepared, a metal acetate/alkoxide solution containing constituent metal species in the appropriate ratio is mixed with an oxalic acid/n-propanol precipitant solution. An oxalate coprecipitate is instantly formed upon mixing that quantitatively removes the metals from solution. Most of the process development was focused on the synthesis and processing of niobium-substituted lead zirconate titanate with a Zr-to-Ti ratio of 95:5 (PNZT 95/5) that has an application in neutron generator power supplies. The process was scaled to produce 1.6 kg of the PNZT 95/5 powder using either a semi-batch or a continuous precipitation scheme. Several of the PNZT 95/5 powder lots were processed into ceramic slug form. The slugs in turn were processed into components and characterized. The physical properties and electrical performance (including explosive functional testing) of the components met the requirements set for the neutron generator application. Also, it has been demonstrated that the process is highly reproducible with respect to the properties of the powders it produces and the properties of the ceramics prepared from its powders. The work described in this report was funded by Sandia's Laboratory Directed Research and Development Program.

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Introduction

Neutron generator power supplies require two ferroelectric ceramic materials, specifically, niobium-substituted lead zirconate titanate with a Zr-to-Ti ratio of 95:5 (PNZT 95/5) and PNZT 95/5 with a partial substitution of tin for zirconia (PSZT). There are no current U.S. suppliers of these materials, since these PZT formulations are unique to the neutron generator application. In anticipation of future needs by Sandia production, this project was undertaken to develop a new, more reliable process for preparing these ceramic materials. Particular emphasis was placed on the PNZT 95/5 formulation. Based on our past experience, in which we have successfully developed and transferred to industry chemical preparation processes, the process developed to prepare PZT powders utilizes the solution chemistry approach.

Both traditional mixed oxide and chemical methods are used for producing perovskite-type ABO_3 oxide powders, including PZT [$Pb(Zr_{1-x}Ti_x)O_3$, $0,<x<1$; where $A=Pb$ and $B=Zr,Ti$]. The most common method for preparing these ferroelectric materials is the mixed oxide process where the individual oxide forms of the constituents (e.g., for PZT: PbO, TiO_2, and ZrO_2) in the desired ratio are mixed. The mixture is then heated in a process known as calcination to convert the constituent oxides into the desired perovskite phase [1]. The perovskite phase is formed by the thermally induced diffusion and reaction of the component oxides to form the more thermodynamically stable complex oxide phase.

In the mixed oxide process, it is difficult to obtain a powder material having a uniform composition and the powder material obtained may contain unwanted phases such as pyrochlores, zirconia, titania, and lead oxide. To reduce the amount of unwanted phases and increase the amount of the desired perovskite phase, high calcination temperatures are often used, causing the powder material to coarsen by formation of hard agglomerates due to partial sintering. Further crushing and mixing are then required to obtain fine-particle material necessary for many applications. The step of recrushing and remixing not only increases the manufacturing cost but also reduces the reliability of the final product by introducing impurities that are incorporated into the calcined product.

Because of the difficulty in controlling compositional homogeneity, powder particle size, and the uniform incorporation of low level dopants by the mixed oxide method, alternate approaches of powder preparation have been developed. The alternate methods are chemical preparation processes that have been developed based on the use of solutions containing some or all of the A-site and B-site components of the oxide to be prepared. The solution approach allows for better mixing of the constituents, less dependence on the source of the constituents, and the possibility of producing a much finer powder with more uniform properties. The chemical preparation process is often a coprecipitation method in which a mixed solution of all of the components which constitute the desired perovskite phase is prepared, a precipitate-forming liquid such as an alkali is added for effecting coprecipitation, and the precipitate is separated out, dried, and calcined. The solutions used in the chemical preparation process can be aqueous or nonaqueous solutions as well as sol-gels and slurries [2-5].

It would be most desirable, for the routes based on precipitation, to have a process that is simple with respect to the number of solutions that need to be mixed to form the precipitate. The solutions used would be as concentrated a possible in order to minimize waste generation. In such a process, one solution could contain all of the A and B

components of the oxide to be produced and a second solution would contain a precipitant. Mixing of the two solutions would quantitatively remove the A and B solution species without the addition of a third solution, for example, to adjust pH. The supersaturation driving force would be extremely high in order to minimize residence time effects often encountered in process scale-up. The precipitate product would be readily filterable and require little or no washing before drying. The dried precipitate powder would be easily converted by calcination to the desired perovskite phase at moderate temperatures where subsequent milling and calcination steps are not required. The resulting oxide powder would be phase pure and reactive to sintering for the subsequent formation of ferroelectric ceramic materials. The process developed in this work and described in the next section was designed with these attributes in mind. In addition, it was a major goal of the project to demonstrate that PNZT 95/5 prepared by the newly designed process would meet neutron generator power supply requirements.

Process Overview

The process developed in this work, known as the Sandia Process (Figure 1), involves the preparation of two homogeneous, clear solutions that contain the four metal ions required to make PNZT 95/5. One, the alkoxide solution, contains Zr, Ti, and Nb. The other, the lead acetate solution, contains Pb. The two solutions are combined to form a homogeneous, clear solution called the metal cation solution. This solution is mixed and then added to an oxalic acid/n-propanol precipitant solution which induces the precipitation reaction. The resulting precipitate is filtered, dried, and calcined to yield the desired PNZT powder. At present the Sandia Process has been used to prepare up to 1.6 kg batches of PNZT powder using 13 liters of liquid reactants and solvents. The details of the synthetic process are described in the **Preparation of a 1500g Batch** section.

```
┌─────────────────────┐      ┌─────────────────────┐
│   Lead Acetate      │      │  Zr, Ti, Nb Alkoxides │
│ + Glacial Acetic Acid │      │ + Glacial Acetic Acid │
└─────────────────────┘      └─────────────────────┘

              ┌──────────────────────────────────┐
              │       Metal Cation Solution       │
              └──────────────────────────────────┘
┌──────────────┐
│ Oxalic Acid/ │                                       Filter
│  n-Propanol  │                                        Dry
└──────────────┘
              ┌──────────────────────────────────┐
              │       PZT Precursor Powder        │
              └──────────────────────────────────┘
                                                      Calcine
              ┌──────────────────────────────────┐
              │         PZT Oxide Powder          │
              └──────────────────────────────────┘
```
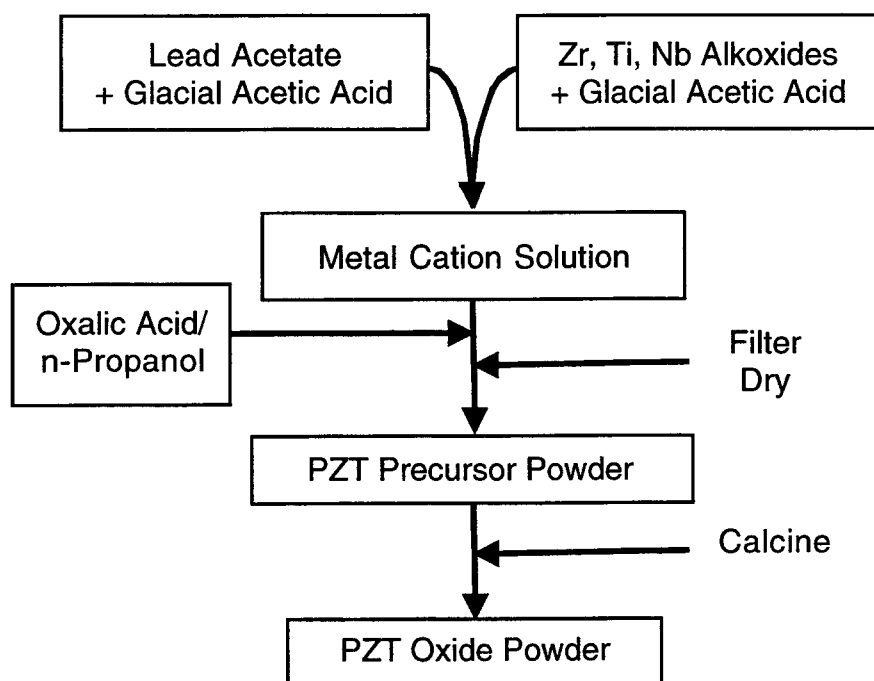
Figure 1. Process flow diagram for the Sandia Process for the preparation of PZT 95/5 powder.

The development of the Sandia Process went through several stages. Initially, work was done at a very small scale (20 ml solution quantities) exploring a wide variety of metal precursors, precipitants, and solvent systems. The results of these experiments and the reasoning used in the selection of the chemical system are described in the next section (**Choice of Reagents**). Having selected the chemical system, the process was scaled to batch sizes that produced 50 to 400g quantities of calcined powder. A set of baseline experimental conditions were established that generally produced a highly filterable precipitate product. These conditions were not optimized and occasionally batches were prepared with undesirable characteristics, such as difficult to filter precipitate slurries. To improve process reproducibility and powder characteristics, a statistically designed study was undertaken investigating a number of processing variables (see **Screening of Processing**

Parameters). The results of this study were used to establish a new baseline for experimental conditions. The revised process was then scaled to batch sizes that produce from 1 to 1.6kg of oxide powder (see **Preparation of a 1500g Batch**). The advantages of the Sandia Process include:

- atomic level mixing of all four metal ions in single solution,
- no pH adjustments are needed,
- all metals can be essentially quantitatively precipitated in less than 2 h,
- the precipitate is not washed,
- the precipitate powder is not spray/freeze dried,
- can be done with 99+% yield (metal basis),
- can vacuum filter slurry normally in 1-2 hours,
- yields a dry precursor powder that breaks up readily,
- requires about 2 gallons of liquid per kilogram of PNZT,
- lends itself to varying formulations readily.

The potential disadvantages of the Sandia Process include:

- the solution that contains all four metals is stable for only a few hours,
- metal alkoxides (Zr, Ti, Nb) can be humidity sensitive,
- the Pb acetate solution appears to be sensitive to water,
- must prepare the liquid lead acetate source from PbO,
- uses organic solvents and must be done with ventilation.

From a synthesis standpoint, the largest potential disadvantage of the process is that solutions are made fresh for each large powder batch. However, the Zr, Ti, Nb metal alkoxide solutions have been shown to be stable for more than one month, the lead acetate solutions for several months, and the oxalic acid/n-propanol solution should be stable indefinitely. Thus solutions could be prepared ahead of time, stored, and combined on the day of the reaction if so desired.

Precautions must be taken when using the alkoxide precursors for Zr, Ti, and Nb, which are known to be sensitive to hydrolysis from ambient humidity. So far, limited sensitivity to humidity of the alkoxide and metal solutions has been observed (laboratory humidity has ranged from 20 to 50 % depending on the time of the year). A thin skin is sometimes seen on top of the alkoxide solution, but this dissolves when the alkoxides are added to the lead acetate. A skin is also sometimes observed on the top of the metal cation solution. To minimize skin formation, the metal cation solution is stirred under a nitrogen atmosphere during aging and while it is being pumped into the oxalic acid solution.

The use of organic solvents dictates that the process be done in a hood. In addition, from an ES&H standpoint, it is standard practice, whether using an aqueous-based or organic-based chemical preparation approach, to perform the syntheses in a well ventilated, contained area owing to the use of lead in the process. The process yields a powder, that when broken up from its dried, chunky texture, results in a dusty powder that is a possible inhalation hazard. All handling is done in a hood, which again is standard practice for a lead-based material no matter what the characteristics of the powder.

Process Development - Choice of Reagents

PZT powder and films have been synthesized previously with a wide variety of techniques and a diverse set of reagents. Synthetic techniques include coprecipitation followed by auto-combustion or calcination; hydrothermal synthesis; direct mixture and firing of the oxides; or sol-gel syntheses (for films). Syntheses can be done in aqueous solvents or nonaqueous solvents, such as ethanol, methanol, 2-methoxymethanol, and 2-methoxyethanol. Lead sources include the acetate, oxide, nitrate, methoxide, or carboxylate. Generally Pb(II) acetate is preferred. Titanium sources include alkoxides, salts, and chelated complexes such as the isopropoxide, methoxide, nitrate, or acetylacetone (acac) complex. Zirconium sources also include alkoxides, salts, or chelated complexes, such as the butoxide, propoxide, methoxide or acac complex.

There are at least two reports [6,7] of coprecipitation with oxalic acid and a proprietary process under development at AWE, Aldermaston in the U.K. Sandia (S. J. Lockwood, S. M. DeNinno, Dept. 1492) is also currently working on a modified version of the U.K. process. The two reported in the literature are Rao et al. [6] in which aqueous salt solutions are coprecipitated using oxalic acid and then calcined at 850 °C, and Potdar et al. [7] in which lead nitrate is reacted with sodium zirconyl oxalate, and potassium titanyl oxalate to form a stoichiometric precursor.

For the Sandia Process, as discussed in the previous section, we use a homogeneous molecular metal cation solution and precipitate it with an essentially nonaqueous oxalic acid solution. The reasoning used for the selection of reagents used for the new process is discussed below.

Zr, Ti, Nb Sources – Metal Alkoxides

Alkoxides were used as they are a convenient molecular source of metal ions that can be mixed with the lead acetate solution to make a homogeneous solution. The n-butoxides of each metal were used as they are less susceptible to hydrolysis than propoxides or ethoxides; they also had the lowest concentration of impurities of the alkoxide sources examined (comparison of Ti and Zr n-butoxides to the n-propoxides of both metals); and by using the same alkoxide source, unwanted alkoxide exchange reactions are avoided.

Alkoxide/Acetic Acid Solution

Acetic acid is added to the alkoxides to provide some prereaction of metals through acetate exchange and polynuclear bridging of acetate groups. Numerous reports of homonuclear [8,9,10,11] (e.g. $Ti_6O_4(OCH(CH_3)_2)_{16}$-4n$(O_2CCH_3)_{4n}$ and polynuclear [12] alkoxide/acetate complexes (e.g. $Zr_6Ti_3(OCH_2CH_2CH_3)_{16}$ $(O_2CCH_3)_8O_6)$ are known (formed via a metathesis, esterification, hydrolysis, oxolation pathway). The prereaction of the alkoxides is important as, in small scale (1-3 g) trials, the titanium n-butoxide and niobium n-butoxide were much less reactive in the oxalic acid solution than the zirconium n-butoxide. For effective removal from solution it is important that the titanium and niobium can complex with the zirconium source and form a reactive heteronuclear complex.

Extensive trials with acetic acid to alkoxide ratios between 0 and 4 showed that the ratio affects the stability of the solution. The solution remains stable when mixed in air for

the longest times (several hours to several weeks) when the ratios are between 0.5 and 2.0. A ratio of 1.0 was chosen as baseline.

Lead Source - Lead Acetate Solution

Lead acetate is a convenient source of highly concentrated lead (>40 wt% Pb) that is prepared by dissolving PbO in glacial acetic acid, resulting in a clear homogeneous solution that is compatible with the alkoxide solution.

Precipitant Solution - Oxalic Acid/n-Propanol

Oxalic acid and lactic acid were investigated for use as possible precipitating agents. It was found early in the project that oxalates formed a much more filterable coprecipitate than did their lactate counterparts. Using ICP analysis of the filtrates from precipitation reactions and performing a constituent metal mass balance, it was demonstrated that oxalic acid can precipitate all four metal ions nearly quantitatively (see **Appendix B**). Oxalic acid can be made in concentrated solutions with nonaqueous solvents (20-25 wt%). In choosing the particular organic solvent, an important criteria was the stability of the metals solution constituents with the solvent; the oxalate species should force the metals out of solution, not their incompatibility with the solvent. A variety of simple alcohols were investigated as possible candidates as the oxalic acid solvent, including methanol, ethanol, n-propanol, isopropanol, and n-butanol. N-propanol was chosen because it formed the most stable, clear solutions when it is mixed with either the metal n-butoxides or the lead acetate solution.

Screening of Processing Parameters

Plackett-Burman Matrix

Preliminary trials on 400 gram or smaller batches led to a baseline process that had a relatively poor reproducibility in terms of precursor powder filterability and agglomeration. A Plackett-Burman matrix approach [13] based on balanced incomplete blocks, was used to determine the main effects of process variables on powder filterability and agglomeration for 100 g batches (Table 1a). Fourteen trial powder batches (designated: SP3x-1, where SP refers to the Sandia Process, 3 is the powder series, x is replaced with a capital letter referring the specific powder batch, and 1 refers to batch size = batch size in grams divided by 100), were used to investigate the effects of 11 variables. High (+) and low (-) values were chosen for each of the variables, as shown in Table 1b. The order of experiments was randomized, and the 7th experiment was repeated to establish reproducibility. Two evaluation criteria were used to quantify the results of each experiment: the filterability of the powder (F#) and the agglomeration of the dried powder (P#), as described in Table 2. The effects of each variable on these properties are summarized in Table 3. The effects were determined from the formula:

$$X = \Sigma R_+ + \Sigma R_- ,$$

where X is the overall P# for each variable or the overall F# for each variable. Thus, to find the P# for variable 1, the P#s for each of the 14 experiments, with the appropriate sign, as indicated in Table 1a, were summed. The magnitude of the number is a measure of the relative significance of the variable, and the sign indicates whether the high or low value of the parameter leads to a better product. E_a is the overall effect of a variable as determined by taking the average of the P# and F# for that variable. So, for example, for alkoxide mixing time it is advantageous to both the filterability and powder properties to mix for 5 minutes rather than 30 minutes.

Table 1a. Plackett Burman Matrix for Screening of Process Variables in the Sandia

Trial	order	1	2	3	4	5	6	7	8	9	10	11
SP3A-1	13	+	+	−	+	+	+	−	−	−	+	−
SP3B-1, M, N	1,7,14	+	−	+	+	+	−	−	−	+	−	+
SP3C-1	9	−	+	+	+	−	−	−	+	−	+	+
SP3D-1	10	+	+	+	−	−	−	+	−	+	+	−
SP3E-1	12	+	+	−	−	−	+	−	+	+	−	+
SP3F-1	6	+	−	−	−	+	−	+	+	−	+	+
SP3G-1	2	−	−	−	+	−	+	+	−	+	+	+
SP3H-1	11	−	−	+	−	+	+	−	+	+	+	−
SP3I-1	4	−	+	−	+	+	−	+	+	+	−	−
SP3J-1	8	+	−	+	+	−	+	+	+	−	−	−
SP3K-1	3	−	+	+	−	+	+	+	−	−	−	+
SP3L-1	5	−	−	−	−	−	−	−	−	−	−	−

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Table 1b. Plackett Burman Matrix of Values of Process Variables

Trial	Order	1	2	3	4	5	6	7	8	9	10	11	P#	F#
SP3A-1	13	30	30	15	20	70	1.5	1	2.5	off	17.7	C	1	1
SP3B-1,M,N	1,7,14	30	10	90	20	70	0.5	1	2.5	on	10	V	3,1,1	5,2,?
SP3C-1	9	5	30	90	20	50	0.5	1	4.0	off	17.7	V	5	5
SP3D-1	10	30	30	90	10	50	0.5	7.2	2.5	on	17.7	C	2.75	2
SP3E-1	12	30	30	15	10	50	1.5	1	4.0	on	10	V	4	2
SP3F-1	6	30	10	15	10	70	0.5	7.2	4.0	off	17.7	V	1	1
SP3G-1	2	5	10	15	20	50	1.5	7.2	2.5	on	17.7	V	2	1
SP3H-1	11	5	10	90	10	70	1.5	1	4.0	on	17.7	C	4.7	4
SP3I-1	4	5	30	15	20	70	0.5	7.2	4.0	on	10	C	4.9	5
SP3J-1	8	30	10	90	20	50	1.5	7.2	4.0	off	10	C	4	5
SP3K-1	3	5	30	90	10	70	1.5	7.2	2.5	off	10	V	4.9	4
SP3L-1	5	5	10	15	10	50	0.5	1	2.5	off	10	C	1.5	2

Variables:

No.	Description	Symbol	+	−
1	alkoxide mixing time	t_{Alk}	30 min	5 min
2	metal solution mixing time	t_{metals}	30 min	10 min
3	precipitate mixing time after t_{thin}	t_{precip}	90 min	15 min
4	time to add metal soln. to oxalic acid soln.	$t_{metal\ add}$	20 min	10 min
5	oxalic acid temperature	T_{OA}	70 °C	50 °C
6	acetic acid to alkoxide ratio	AA:Alk	1.5	0.5
7	water to PNZT ratio	H_2O:PNZT	7.2	1
8	oxalic acid to metal ratio	OA:metal	4.0	2.5
9	external heat (on/off at start of metal addn.)	heat	on	off
10	oxalic acid concentration	[OA]	17.7 wt%	10 wt%
11	precipitate stirring speed	speed	variable	constant

Table 2. Evaluation Criteria for SP Samples

P# (Powder Agglomeration)	F# (Filterability)[1]	
	Not shear mixed (2L medium frit funnel)	Shear mixed (3L medium frit funnel)
1 - hard, compact; but breakable	1 - not filterable	1 - not filterable
2 - large chunks; breakable	2 - >60 minutes	2 - > 120 minutes
3 - readily breakable; some chunks	3 - 10-30 minutes	3 - 60-120 minutes
4 - flows well with some small chunks	4 - 5-10 minutes	4 - 30-60 minutes
5 - collapses to "free-flowing" powder	5 - < 5 minutes	5 - < 30 minutes

1 = Times refer to the time at which the top of the cake is dry (not shear mixed) or the time the cake pulls away from the sides of the funnel (shear mixed).

The overall effects of each variable, along with confidence levels from a t-test, are presented in Table 3. The most significant variables are: alkoxide mixing time, metal solution mixing time, mixing time of the precipitate slurry, oxalic acid to metal ratio, and oxalic acid concentration. The results of the matrix led to several process changes and a new baseline process. Changes from the old baseline process are shown in Table 4.

Table 3. Variables and Effects for SP3 Batches Table

#	Variable	+	−	P#	F#	E_a	Rel. Sig.	t-test
1	alkoxide mixing time	30 min	5 min	-8.2	-6.5	-7.4	7.96	95%
2	metal soln. mixing time	30 min	10 min	7.4	2.5	4.9	5.27	90%
3	precip. mixing time	90 min	15 min	9	11	10	10.75	95%
4	metal addition time	20 min	10 min	0	1.9	0.9	0.97	−
5	oxalic acid temperature	70 °C	50 °C	-0.8	0.5	-0.2	0.22	−
6	acetic acid to alkoxide ratio	1.5	0.5	3.4	-2.5	0.7	0.54	−
7	water to PNZT ratio	7.2	1	1.4	-0.5	0.5	0.54	−
8	oxalic acid to metal ratio	4	2.5	9.4	7.5	8.5	9.14	95%
9	external heat	on	off	3	-1.5	0.8	0.86	−
10	oxalic acid conc.	17.7 wt%	10.0 wt%	-4.8	-8.5	-6.7	7.2	95%
11	precip. stirring	variable	constant	0	-3.5	-1.8	1.94	75%

Notes:
- SP3 batches are 100g PNZT batches made by the Sandia Process.
- Effect criteria are determined from the formula
  $$X = \sum R_+ + \sum R_-,$$
  where X is P#, F#, or E_a and R is the rating (1-5) for each sample.
- Relative significance was found by dividing E_a by s ;
  $$s = (\sum E_a(x)^2 /n)^{1/2}$$
  where x = 4, 5, 6, 7, 9, & 11; and n = 6 (thus s = 0.93).

Table 4. Process Changes after SP3 and SP4 Batches

Process Changes
Stir alkoxides + acetic acid for 5 minutes versus 10 minutes.
Stir alkoxides + acetic acid + lead acetate for 30 minutes versus 15 minutes.
Use oxalic acid concentration of 17.7 wt% (as before)
Use temperature of 50 °C with heat on during metal solution addition.

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Establishing a New Process Baseline

Two questions that arose after the matrix study were (1) could precursor powders with F#s and P#s of 5 be achieved by using 17.7 wt% oxalic acid solution, and (2) is there any difference in the F# and the P# if dehydrated oxalic is used versus the dihydrate. In the former case, it is advantageous to use an oxalic acid concentration as great as possible to minimize waste. From the matrix it appears that using a 10 wt% solution is better than using 17.7 wt%. To determine if P# and F# were still optimal with greater than 10 wt% oxalic acid, a 400 g batch (SP4A-4) was made with the new baseline process with 16 wt% oxalic acid. This led to F# and P#s of 5. Given this success, a 400 g batch was made with a 17.7 wt% oxalic solution (SP4B-4) and the new baseline process; this also led to F# and P#s of 5. The baseline process was thus modified to use a 17.7 wt% oxalic acid solution with the understanding that other parameters probably should not be changed, since the process is fairly far from optimal, and a small tweak could result in major changes of F# and P#. Since from the matrix experiments it was found that the use of oxalic acid solution temperatures of 50°C to 70°C had little effect on powder properties, it was decided to use a solution temperature of 50°C. To minimize evaporation of n-propanol and to ease future scale-up of the process where the pumping of the oxalic acid solution would be required, a baseline temperature of 35°C was established in SP11 powder series, with no apparent change in filterability or powder characteristics.

For the latter question, a 400 g batch was prepared using oxalic acid dihydrate (SP4C-4) using the new baseline established in SP4B. SP4B used anhydrous oxalic acid, and thus served as the control for this experiment. SP4C led to an F# of 4 and a P# of 4.5. Little difference was noted between the preparation SP4B and SP4C, thus, the baseline process now uses dehydrated oxalic acid for ease of handling and greater solubility in n-propanol.

The most critical factors to producing filterable, easily handleable powders is the oxalic acid to metal ratio and the concentration of the precipitate in the final solution. In the former case, it is important to use a ratio greater than or equal to that needed for stoichiometric reaction of oxalic acid with the metal ions (3.1 for our process). We thus changed the baseline process to use a ratio of 3.5, which gives an excess but generates less waste than 4.0. In the latter case, it is important to not evaporate too much of the n-propanol. In several cases, especially with n-propanol to PNZT powder ratios of 7 or less, evaporation at 50°C or 70°C was significant enough to evaporate 10 to 20% of the initial n-propanol. In many of these cases, especially if the other variables were far from optimal, unfilterable, precipitate slurries resulted. Thus, there is a balance between powder filterability and waste generated that is controlled by the amount of n-propanol used.

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Process Scale-Up (400g to 1500g Batches)

Establishment of a Reliable Method of Preparing Pb Acetate

The lead acetate solution should be clear (the solution color can range from colorless to pale peach or pale yellow). There are four problems that have been observed in the lead acetate preparation: (1) the presence of black particles in the solution, (2) the presence of reddish brown particles, (3) the solution turns translucent green/gray, (4) a white precipitate forms in the solution. From EDX the black particles are lead metal and an iron-containing impurity. They can be removed by decanting the solution or using a PbO source that does not contain these impurities. The use of the Hammond Lot 6130 source has minimized this problem and is now the standard source. The reddish color is owing to suspended Pb_3O_4. To eliminate this, 0.01 moles acetyl acetone is added per mole of lead to dissolve the Pb_3O_4. The green/gray color is potentially due to the presence of transition metal impurities introduced by using metal utensils or stirrer, or due to the presence of a small amount of water. Only glass and Teflon labware are now used. The white precipitate is likely solid lead hydoxyacetate and is observed when the solution sits for a longtime (several weeks) or when processes that introduce water are used (e.g. the solution is stirred in air for more than several days; or a non-fresh source of glacial acetic acid is used).

Determination of an Optimum Level of Excess Pb (SP6 Powder Batch Series)

Early high-fires appeared to show that densification occurred at lower temperatures and to acceptable extents when 6% excess lead was used, but not 3% or 0%. The work at Sandia on modifying the U.K –developed process has been shown to achieve acceptable densities using 0% - 1% excess lead. These results prompted a careful reexamination of earlier data. It now appears, by improving our ability to minimize lead loss during firing, that acceptable densities may be achieved with less than 6% excess lead. The SP6 series of batches were prepared with 0%, 1%, and 3% excess lead for use in sintering studies performed. The conclusions from these studies are that high fired slugs that meet specifications can be made using 0.5 to 1% excess lead.

Vary Zr/Ti Ratio to Determine Depoling Pressure Curve (SP7 Powder Batch Series)

These batches were prepared to produce a calibration curve for depoling pressure, so that the Zr/Ti ratio can be chosen to give optimal depoling characteristics. 1500 g preparations were made with 1% excess lead and Zr/Ti = 94.8/5.2 (A), 94.2/5.8 (B), 95.4/4.6 (C), 93.8/6.2 (D), 94.5/5.5 (E, F). A preliminary depoling pressure versus %Ti plot was generated using ceramics prepared from this powder series.

Optimize Mixing to Break Up/Eliminate Large Agglomerates (SP8 Powder Batch Series)

In early batches, previous to SP8A, a 10" U-shaped overhead stirrer operating at ~80 rpm was used to provide agitation in the reaction beaker. As shown in Figure 2, this results in an induction period in which the temperature of the reaction mixture is constant until all of the metal solution is pumped into the oxalic acid solution. After this time the temperature typically rises 4 to 6°C. The hot plate is turned off after all of the metal solution is added, so

the temperature rise is ascribed to the exothermic reaction of the metal precursors with the oxalic acid and subsequent heteroatomic condensation reactions. The solution becomes markedly more viscous at $t/t_{addition} \sim 1.0$, as indicated by the sharp maximum in the torque exerted by the stirrer. With the overhead stirring method, the particles are quite large and filtration occurs very rapidly, sometimes within 5 minutes of adding the solution to a 3 L funnel. The drawback is that large agglomerates ($> 30 \, \mu m$) are commonly observed in the calcined powder.

In batches SP8A and later, a shear mixer was used along with the 10" U-shaped stirrer to provide a better mixing of the precursor powder. A 300 g batch with 1% excess lead, Zr/Ti = 94.8/5.2, and shear mixing only led to a powder that was difficult to filter (F# = 2) and was relatively hard (P# = 2.5). The precipitate was mixed for only 15 minutes after all of the metals were added to the oxalic acid solution. The next batch (SP8B-13) used shear and overhead mixing. The metal solution was injected under the surface of the oxalic acid solution, near the shear mixer. The shear mixer was employed only during the time the metal solution was being pumped into the solution. A major difference in the optical appearance of the slurry, the solution temperature versus time, and torque of the overhead stirrer versus time were observed. The solution was immediately opaque and quite white with the shear mixer, as compared to a translucent with the overhead stirrer only.

The temporal evolution of heat evolved and torque at the stirrer are shown in Figure 3. The rise is again 4 to 6°C, but the rise is linear and starts at $t/t_{addition} = 0$. This indicates the reaction with the oxalate is occurring much more rapidly when using the shear mixer, undoubtedly owing the much smaller particle size and thus higher surface area to volume ratio of the metal solution droplets. The minimal torque indicates a dramatic difference in solution rheology with the shear mixer. The aggregation of primary particles at this stage in the reaction is expected to be much less with the shear mixer than with the overhead stirrer alone.

The precursor slurry was stirred for 90 minutes after all of the metal solution was added. The precursor powder was done filtering in about 30 minutes (cake pulled away from sides) as compared to about 15 minutes for the process with only overhead stirring. The product was assigned an F# of 4. The dried powder was given a P# of 3.5. The combination of using a shear mixer during addition of metals solution to the oxalic acid/n-propanol precipitant solution and the U-shaped mixer during for the entire precipitation/aging process has been adopted as baseline for the Sandia Process.

Large Batches for Explosive Functional Testing (SP9 Powder Batch Series)

Four 1500 g batches with 0.5% excess lead and Ti/Zr = 95/5 prepared for processing into components for explosive functional testing and powder processing studies. The baseline calcination temperature was raised from 775°C to 900°C during this series, based on the results of a calcination/sintering study. Also added during this powder series was dry ball milling of the powder after organic burn out at 400°C. This step was added to breakup weak agglomerates that formed during drying of the precursor powder.

Large Batches of PNZT 52/48 for Direct Fabrication Project (SP10 Powder Batch Series)

Several large batches of PNZT 52/48 powder were prepared (see **Other Formulations** section for details) for use in the Direct Fabrication of Ceramic Components Project at Sandia.
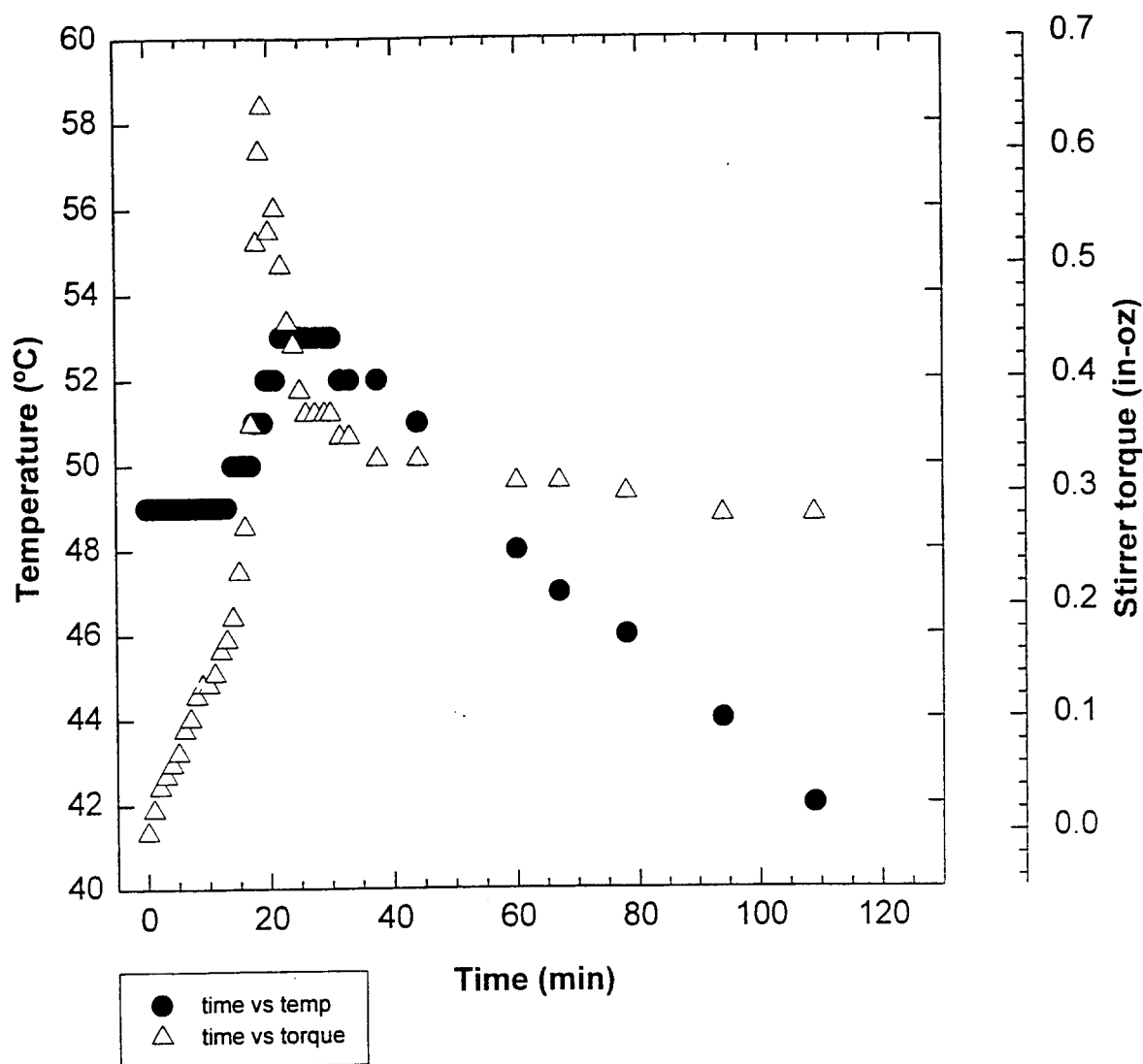
Figure 2.   Temperature and torque versus time for SP6A-15. The 1500 g batch was prepared by pumping the metal solution into the oxalic acid solution and agitating with a 10" overhead stirrer operating at ~80 rpm. The metal solution was pumped in over ~18 minutes. (Note: The maximum in torque and the end of the induction period coincide with the completion of the metal solution addition.) The 4°C temperature rise and the distinct change in rheology with a thickening and then a thinning stage are typical of preparation done with overhead stirring only.
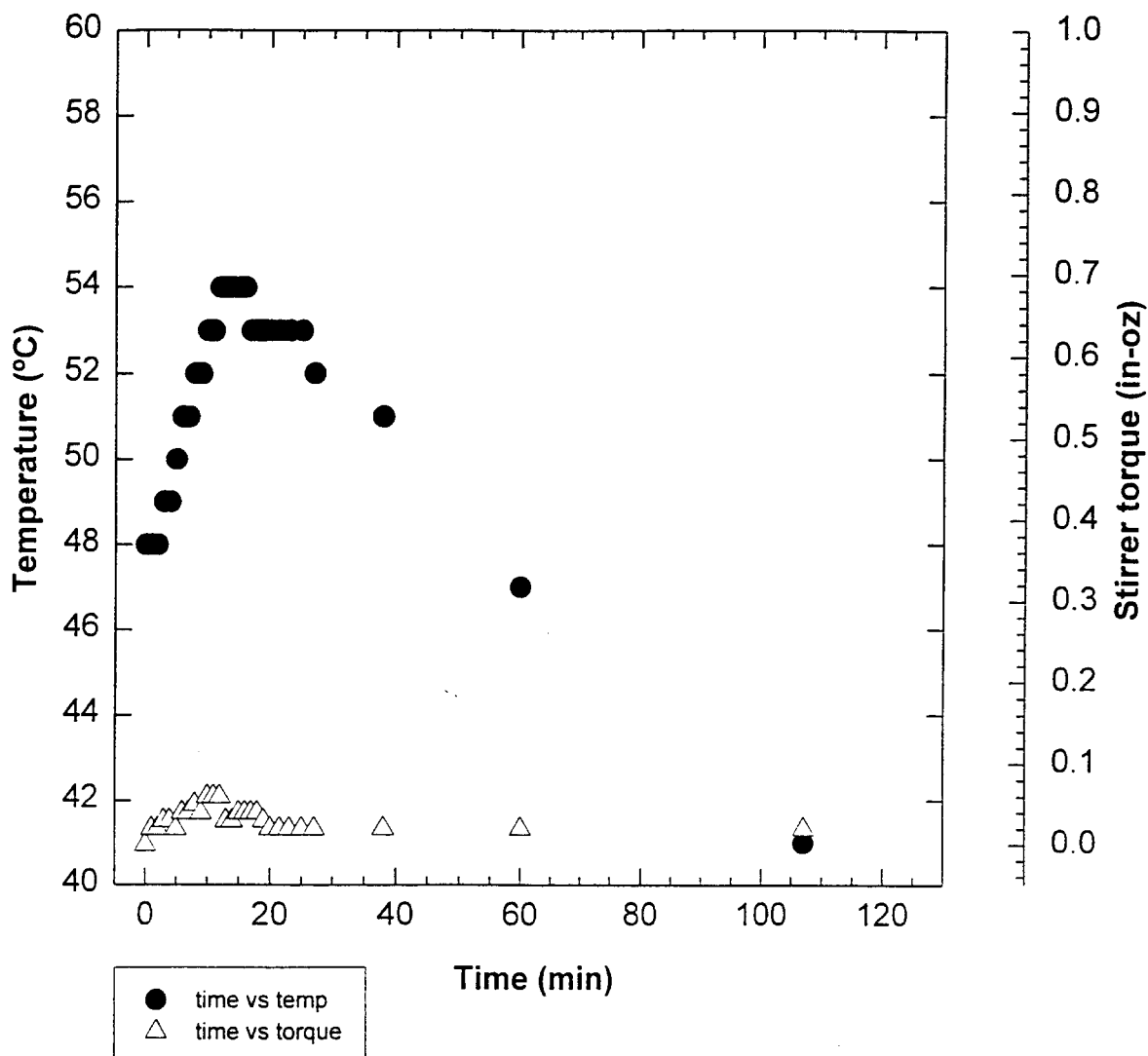
Figure 3.   Temperature and torque versus time for SP8B-13. The 1300 g batch was prepared by pumping the metal solution under the surface of the oxalic acid solution near the shear mixer while agitating with a 10" overhead stirrer operating at ~55 rpm. The shear mixer was turned off immediately after the metal solution addition was complete. (Note: the linear temperature increase and the very low torque values.) The thickening is not seen when the shear mixer is used.

Large Batches for Explosive Functional Testing (SP11 Powder Batch Series)

Nine 1500g batches with 0.5% excess lead and Ti/Zr = 95.7/4.3 were prepared for processing into components for explosive functional testing and powder processing studies. The oxalic acid solution temperature was reduced from 50°C to 35°C during this series. Also, the hold time of the 400°C pyrolysis step was standardized to 16 hours.

Large Batches for Explosive Functional Testing (SP12 Powder Batch Series)

Nine 1500 to 1600g batches with 0.5% excess lead and Ti/Zr = 95.6/4.4 prepared for processing into components for explosive functional testing and powder processing studies. During this powder series the influence of 500 to 1200 ppm levels of Al on functional test performance was investigated. Also it was in this powder series where a study was made to reduce the size or eliminate the source of zirconia-rich inclusions that had been noted in powder compacts and sintered material (SEM analysis by B. McKenzie, 1822). The source of these inhomogeneities was traced to the formation of particles by pre-hydrolysis of zirconium n-butoxide. To reduce the size or eliminate these particles, the shear intensity was increased and a 5 micron filter was added to the metal solution feed line. The results of the Al impurity and Zr-inclusion work will be published in a subsequent SAND Report when all of the characterization data has been collected and analyzed.

Continuous Precipitation Process (SPC Powder Batch Series)

Two 1300g batches with 0.5% excess lead and Ti/Zr = 95.6/4.4 were prepared by a continuous modification of the baseline batch process. This work was done to demonstrate the feasibility of preparing PZT powders by a continuous process based on the Sandia Process chemistry. The continuous processing approach has many inherent advantages with regard to process scale-up.

Preparation of a 1500 g Batch

The number of grams for all batches, regardless of lead content, refers to the number of grams of $Pb_{0.991}(Zr_{0.95}Ti_{0.05})_{0.982}Nb_{0.018}O_3$ (PNZT) the reaction yields. For a 1500 g batch, there will thus be (1500 g/342.448 g/mol) = 4.3802 moles of PNZT. See **Appendix C** for a sample SP synthesis sheet.

Lead Acetate Preparation

See **Appendix D** for a sample lead acetate preparation sheet. For a 0% excess lead solution, 968.82 g of high purity lead (II) oxide (yellow PbO), as calculated from:

moles PbO = 4.3802 moles PNZT/1500g PNZT * (0.991 moles PbO/mol PNZT)
= 4.3408 moles/1500g PNZT

or,

grams PbO = moles PbO * 223.19 g/mol = 4.3408 mol * 223.19 g/mol = 968.8 g

is mixed with glacial acetic acid. The target acetic acid to lead ratio is 4.0. Generally a 1.2 to 1.5 times excess is used. So, for an acetic acid excess factor of 1.2 times, 1251.2g acetic acid is used as calculated from:

grams acetic acid = 1.2 * 4.0 moles AA/mol PbO * 4.3408 moles PbO/1500g PNZT *
60.05g AA/mol AA = <u>1251.2 g/1500g PNZT</u>

Initially, the kettle is charged with all of the dry PbO powder. Glacial acetic acid is slowly added to the kettle with the evolution of much heat and vapor. At first just enough acetic acid is added to cover the lead oxide. After the bubbling subsides, additional acid is added and the skeletal yellow PbO cake is broken up with a Teflon rod. The acid is added in 4 or 5 aliquots over the course of about 30 minutes. The cake is slowly broken up into small pieces. The solution becomes progressively more viscous and turns dark brown/red owing to the presence of red lead (Pb_3O_4). The remaining yellow lead acetate particles are broken up with a Teflon stirrer. After about one hour after the first aliquot of glacial acetic acid is added, the kettle is assembled with the stirrer and lid. The solution is stirred at 50-90 rpm with an overhead stirrer (glass-shafted Teflon stirrer) while under a nitrogen purge for several hours to dissolve all of the yellow lead. When the yellow lead is essentially all dissolved, 4.46 mL acetyl acetone is added to eliminate the red lead, as calculated from:

mL acetyl acetone = 0.01 moles acac/mole PbO * 4.3408 moles PbO/1500 g PNZT *
(100.12 g acac/mol acac) / (0.975 g acac/mL acac)
= <u>4.46 mL acac/1500g PNZT</u>

The red lead dissolves with stirring in less than one day.

The preparation can be done in 1-2 days. It yields a clear, solution that ranges from colorless to pale peach or pale yellow in color. The solution is generally stored in the kettle under a nitrogen blanket until use (within 1-2 days) and remains stable. For longer term storage, the solution is transferred to a container and capped tightly. In this manner, the solution has been known to be stable for up to a year. The final concentration ranges from 0.00191 mol Pb/g solution to 0.00233 mol Pb/g solution depending on the excess acetic acid used and the amount of acid that evaporates.

<u>Alkoxide/Acetic Acid Solution</u>

The n-butoxides of Zr, Ti, and Nb are gravimetrically assayed to determine the metal contents. Zr n-butoxide is analyzed by ICP to determine the concentration of Ti and Hf in the source, and the calculated weights of Zr n-butoxide and Ti n-butoxide are corrected based on this assay (see **Appendix A**). To prepare the alkoxide solution, to a 4 L beaker 4.0629 moles "Zr+Hf" is added, as calculated from:

moles "Zr+Hf" = (0.95 * 0.982) moles "Hf+Zr"/mole PNZT * 4.3802 moles PNZT/1500 g
PNZT = <u>4.0862 moles/1500g PNZT</u>

which generally equates to about 1830 g of Zr n-butoxide; 0.2151 moles "Ti" is added as calculated from:

moles "Ti" = (0.05 * 0.982) moles "Ti"/mole PNZT *4.3802 moles PNZT/1500 g PNZT
= <u>0.2151 moles/1500g PNZT</u>

which generally equates to about 73.60 g Ti n-butoxide (note that the amount of Ti n-butoxide added depends on the concentration of Ti in the Zr n-butoxide); and 0.07884 moles "Nb" is added as calculated from:

moles "Nb" = 0.018 moles "Nb"/mole PNZT * 4.3802 moles PNZT/1500g PNZT
= 0.0788 moles/1500g PNZT

which generally equates to about 33.30 g Nb n-butoxide. To this 263.03 g glacial acetic acid is added as calculated from:

moles glacial acetic acid = 4.0862 moles "Zr + Hf" + 0.2151 moles Ti + 0.0788 moles Nb
= 4.3801 moles/1500 g PNZT * 60.05 g AA/mol AA
= 263.03g/1500g PNZT

Note that the amount of GAA can be from 0.5 to 2.0 times the moles of PNZT, but typically 1.0 times is used. The three alkoxides are weighed directly into the 4-L beaker. The acetic acid is weighed into a Teflon beaker and poured into the alkoxide solution with stirring, which evolves much heat. The alkoxide/solution is covered with a watch glass and stirred with a 3" magnetic stirrer on a stir plate for 5 minutes in air.

Metal Solution

The alkoxide solution is poured into the lead acetate solution over about 30 seconds with overhead stirring at ~120 rpm with the evolution of much heat. Nitrogen is flowed over the metal solution after the alkoxide solution has been added. The metal solution is stirred initially at ~120 rpm until the solution is mixed well (becomes transparent, about 1-3 minutes), then decreased to ~70-90 rpm for the remaining mixing time. A Caframo high torque overhead stirrer equipped with a glass-shafted Teflon stirrer is used.

Coprecipitation of Precursor Powder

A 17.7 wt% solution of anhydrous oxalic acid in n-propanol is prepared in a 25 L Pyrex reaction vessel. To prepare the solution, 1442.2 g anhydrous oxalic acid, as calculated from:

grams oxalic acid = 3.5 moles oxalic acid/mole PNZT * 4.3802 moles PNZT/1500 g
PNZT * 94.07 g/mol = 1442.2g/1500g PNZT

are weighed into a 4 L beaker and transferred to the 25 L reaction vessel. To this 8361 mL n-propanol, as calculated from (assuming the OA contains no water):

mL n-propanol = g n-propanol/0.802 g/mL

where the g n-propanol is calculated based on desired OA weight percent (17.7 in this example),

0.177 = (g OA/ (g OA + g H_2O + g n-propanol)

using the calculated amount of OA and rearranging,

g n-propanol = (1442.2 g - 0.177 * (1442.2 g + 0 g))/0.177 = 6705.9 g

or,

mL n-propanol = 6705.9g/0.802g/ml = 8361 ml

are added to the 25 L reaction vessel. The solution is stirred at about 50 rpm with a 10" U-shaped blade driven by a high-torque Caframo overhead stirrer. The solution is heated to 35°C on a 10" Cole-Parmer Series 04644 Hot Plate equipped with a temperature probe.

The aged metal solution is pumped with a Masterflex 7518-12 pump into the oxalic acid solution at 200 mL/min. The metal solution enters the oxalic acid solution below the level of the oxalic acid solution, the inlet being positioned near the shear mixer head intake. The oxalic acid solution is shear mixed with a Janke & Kunkle Ultra-Turrox shear mixer and stirred with a Caframo overhead stirrer set at about 50 rpm. The shear mixer is set at 50-75 on a Tekmar TR-10 controller. The shear mixer is left on during the time the metal solution is added. After the metal solution is added, the shear mixer is turned off with the overhead stirrer remains on throughout the synthesis.

The addition of the metal solution takes about 18 minutes, after which time the external heat to the hot plate is turned off. The temperature of the precipitated suspension is monitored throughout the reaction. The precipitate is allowed to stir for 90 minutes after the solution thins (or, if no thinning occur, 90 minutes after all the metal solution has been added).

Filtration of Precursor Powder

The white precipitate suspension is pumped at 1.4 to 1.7 L/min with a Masterflex 7529-10 pump loaded with size 73 tubing from the 25 L reaction vessel into four 3-L medium frit funnels. The precipitate is allowed to settle in the funnels without vacuum for 5-40 minutes. The funnel contents are monitored to determine whether any filtrate passes through within this period. In most batches the filtrate begins dripping through within 2-3 minutes. After this initial setting period, the vacuum is turned on. The time for the liquid level to drop below the top of the cake or for the cake to pull away from the funnel sides and/or the cake crack (when the shear mixer is used) is monitored and used to determine the "F#". The powders are generally under vacuum for 1-2 hours. Typically 40 to 50% of the total volume of liquids used in the preparation of a powder batch is collected as filtrate, depending on how long the vacuum is applied. The density of the filtrate generally ranges from 0.84 to 0.88 g/cc. The wet filter cakes are either dried directly in the frit funnel or are transferred to pails (two cakes per ~13 L pail) to be dried at about 88°C for 72-200 hr. depending on oven availability. The powders are removed from the oven, allowed to cool, weighed, and then are pyrolyzed, as described in the next section. Typical apparent yields are 175%, that is, 40-45% of the powder is organic material, depending on the length of oven drying time.

Pyrolysis/Calcination of the Precursor Powder

The white precursor powder is transferred from the funnels to pails (when the filter cakes are dried in the funnels) and the cake broken up to a loose powder with chunks and assigned a P# (see Table 2). Depending on batch size, the powder is transferred to about ten 14 cm x 19 cm x 4 cm tared alumina crucibles for a 400°C pyrolysis step (schedule, Figure 4a). Each crucible is filled with approximately 275 g precursor powder (for a 1.6 kg batch size), after setting aside 15 g of the precursor for archiving. The crucibles are carried to the furnace in a covered plastic container. Two crucibles are placed on each of the four shelves in a Fisher Isotemp Muffle Furnace (650 series, Model 126, chamber 14" L x 12" W x13" H). The remaining two crucibles are placed side by side in the Thermolyne 6000 muffle

furnace (Series 539, chamber size 10" L x 12.75" W x 6.75"). Upon completion of the pyrolysis step, the pyrolyzed material is dry ball milled for 7 hours in a one gallon wide-
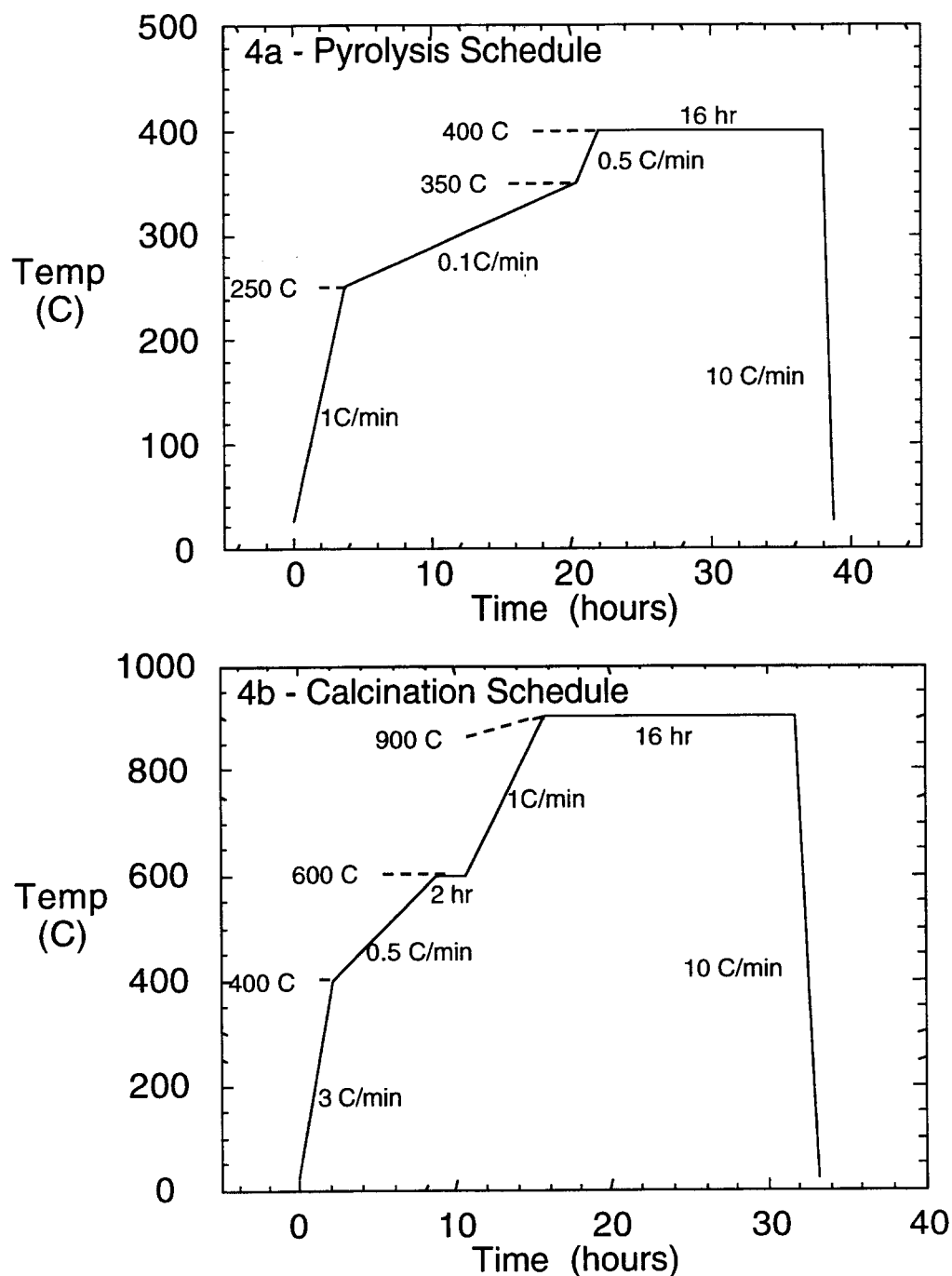
Figure 4.   a: Heating schedule for pyrolysis of dried precipitate powder. b: Calcination schedule for converting pyrolyzed powder to desired oxide phase.

mouthed Nalgene bottle containing 11.2 pounds ZrO_2 media. Separation of the media from the powder is accomplished with the use of an 8 inch No. 10 U.S.A. Standard Sieve (ASTM

designation E11) utilizing a CSC Scientific Sieve Shaker at setting of about 1.5 for 3-5 minutes per sieve loading. A 0.5 g aliquot of post-ball milled pyrolyzed powder is taken for scanning electron microscopy analysis. The powder is then calcined in covered Al_2O_3 crucibles (crucible size described earlier; calcination schedule shown in Figure 4b). After the crucibles have cooled, they are weighed to determine the wt% loss due to calcination . This is typically about 3%. Several aliquots of the calcined sample are then submitted for analyses: <0.1 g for X-ray diffraction; 0.5 g for scanning electron microscopy; 1.2-1.5 g for particle size distribution; and 1.5 g for analytical analysis (ICP).

The calcination schedule and drying schedule for the precursor powders were chosen based on thermogravimetric/infrared spectroscopy (TGA/IR) results and x-ray diffraction analysis. TGA/IR analysis up to 800°C was performed using an atmosphere of flowing air (Figures 5-7). Carbon dioxide, carbon monoxide, and water were the primary decomposition products. A small concentration of hydrocarbons was also observed, for example, trans-2-butene is evolved at approximately 190°C. Esters of acetic acid are detected at approximately 110°C, including 2-ethylbutyl ester acetic acid ($H_3CC=OOCH_2CH(C_2H_5)_2$ and isobutyl ester acetic acid ($H_3CC=OOCH_2CH(CH_3)_2$. These esters remain after (and a presumably formed during) drying the precursor powder at 88°C. The presence of these low volatility esters may explain the slightly different drying losses depending on drying time and temperature. Their formation and volatility depends on drying time and temperature, and thus affects the amount of residual organics in the dried precursor powder.

Method: 10°/min. from 30°to 800°C   Run Date: 18-Nov-96 14:39
Comment: TGA/FTIR   SP2C-1   sample in air   ramp 10°/min. to 800°C
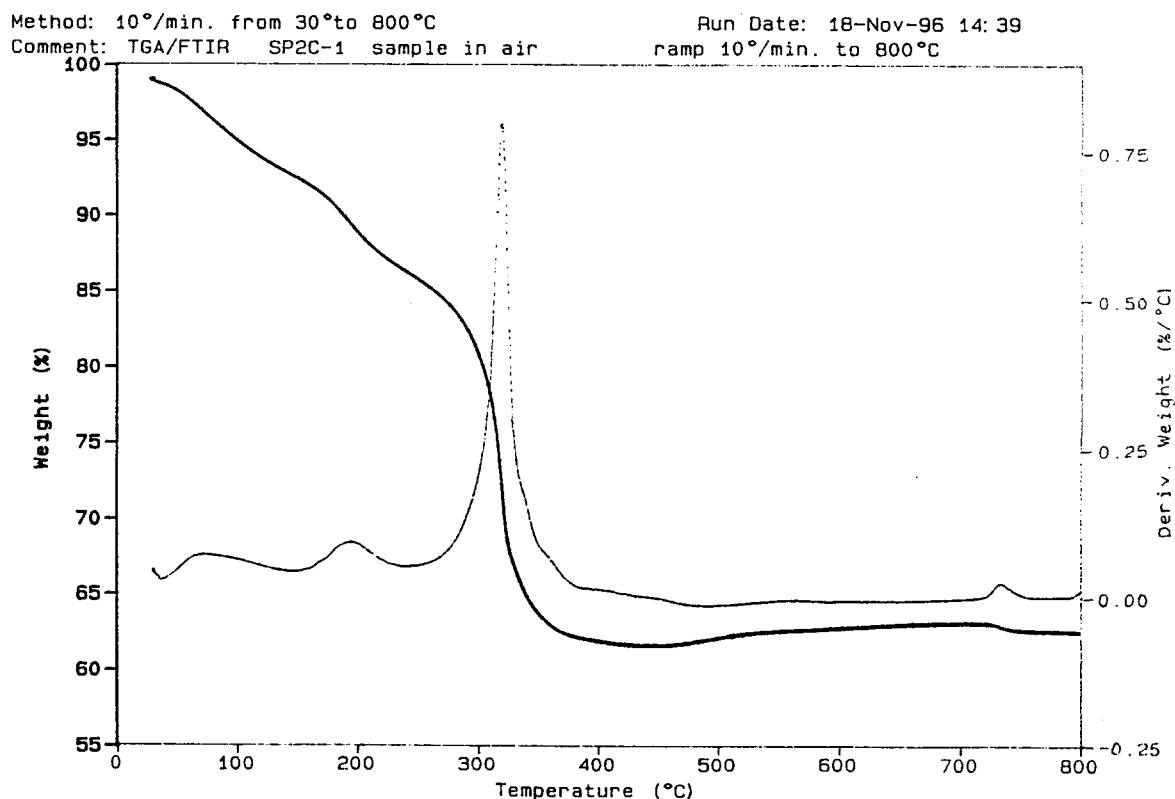
Figure 5.   Thermogravimetric analysis in air of PNZT dried precursor powder SPC2. There is a large exotherm at ~325°C corresponding to a precipitous weight loss. The temperature ramp in the pyrolysis schedule is slowest between 250°C and 350°C to accommodate the large amount of heat evolved between these temperatures.
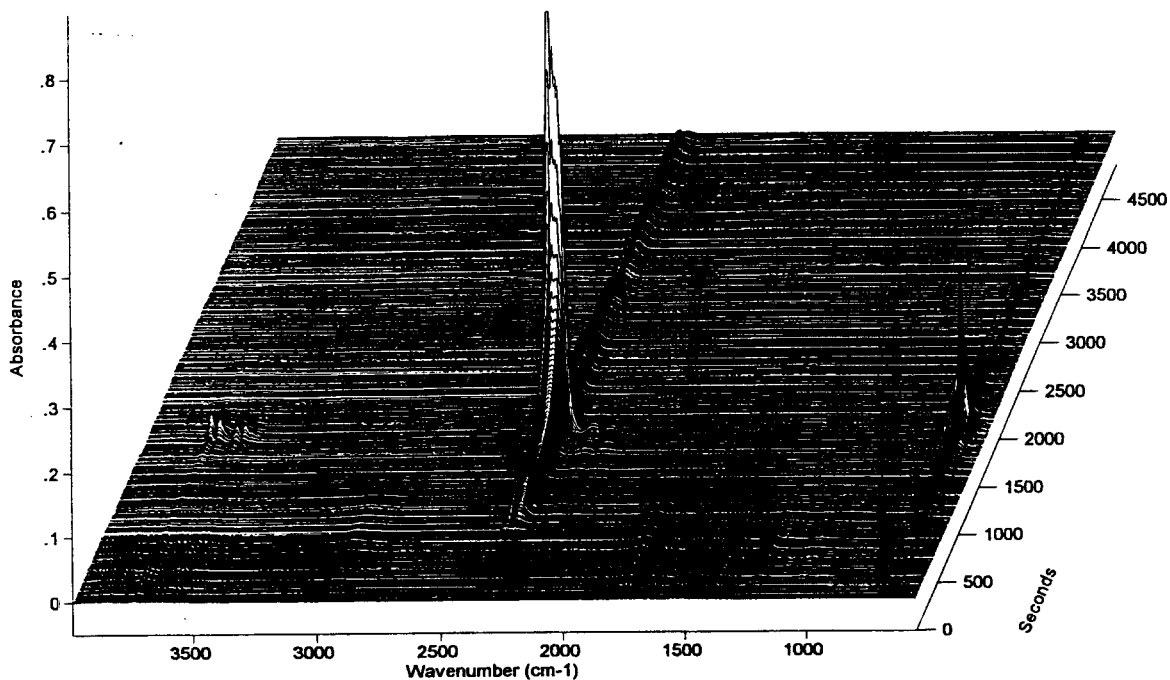
Figure 6. Temporal evolution of infrared spectroscopy versus time (the temperature ramp is 10°C minute from 25°C to 800°C, so the number of seconds can be converted to a temperature from (T = (# of seconds * 1 min/60 seconds * 10°C/min) + 25°C). The peaks correspond to water (>3500 and 1300-2000 wavenumbers), carbon dioxide (2364, 2330, and 650-700 wavenumbers), and carbon monoxide (2177 and 2113 wavenumbers).
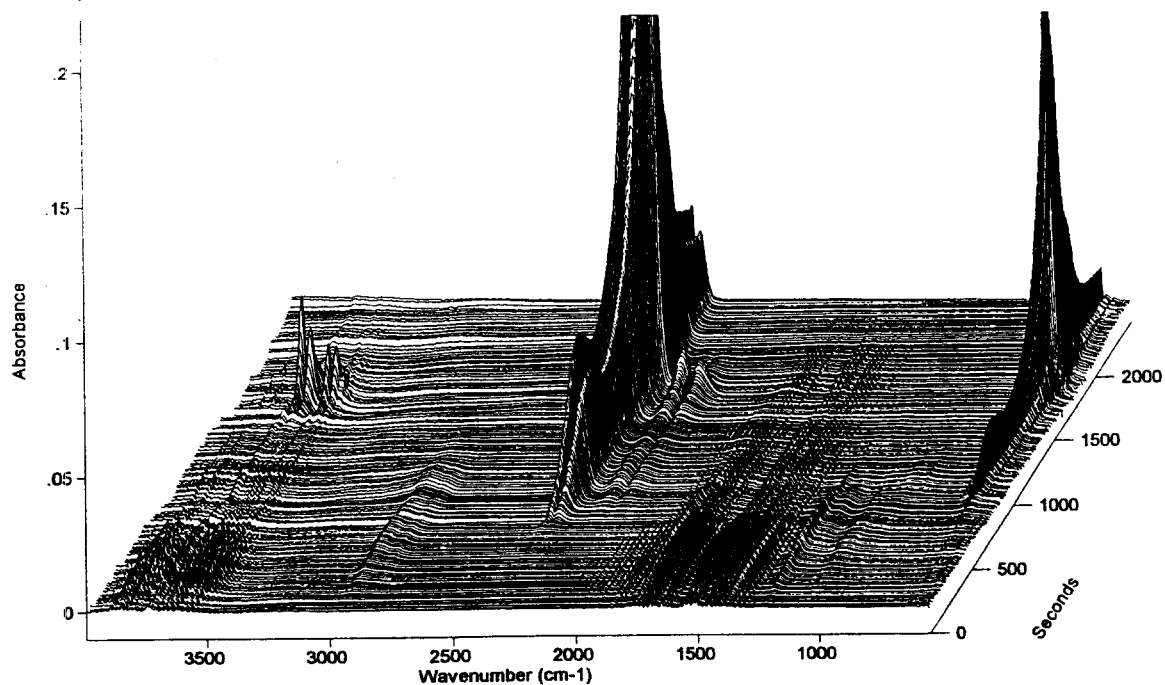
Figure 7. Temporal evolution of infrared spectroscopy versus time (blow-up of early stage presented in Figure 6). The peaks at ~3000 wavenumbers (2966) and from 1000-2000 wavenumbers (1770, 1235, 1039) are indicative of 2-ethylbutyl ester acetic acid and isobutyl ester acetic acid.

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Process Reproducibility and Properties

The batch Sandia Process has continued to evolve during its development as described in the previous section. In this section, the overall performance of the process is assessed with respect to reproducibility of powder properties, densification behavior, electrical response, and performance when explosively functionally tested. The results presented primarily focus on the most recent, fully characterized powder batches at the time of this writing. They deal mainly with the batch SP-12 powder series and continuously precipitated powder SPC series. The discussion deals with the PNZT 95/5 composition that has as its application the voltage bar component in Neutron Generator Power Supplies.

Powder and Ceramic Properties

The powder stoichiometry is measured after calcination using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). The procedure for this analysis was developed in the Analytical Chemistry Department (W.B. Chambers/J.C. Barrera). Table 5 shows a comparison of the ICP analysis of the SP12 powder series and the continuously precipitated SPC powder series. The results show that the ICP results are close to the compositions to which the powders were batched. The footnotes show the ICP Jobs in

Table 5. Powder Composition Data for the SP12 Batch Powder Series and the SPC Continuously Precipitated Powder Series

| Powder Batch #	Batched To:				ICP Results:			
	%Ti in (Zr+Ti)	mole frac Pb	mole frac Nb	Al (ppm)	%Ti in (Zr+Ti)	mole frac Pb	mole frac Nb	Al (ppm)
12A	4.4	0.996	0.018	1000	4.21^1	0.97	0.0184	1190
12B	4.4	0.996	0.018	500	4.25^1	0.98	0.0182	870
12C	4.4	0.996	0.018	0	4.20^1	0.96	0.0185	510
12D	4.4	0.996	0.018	0	4.54^2	1.03	0.0194	480
12E	4.4	0.996	0.018	0	4.52^2	1.02	0.0196	470
12F	4.4	0.996	0.018	0	4.48^2	1.01	0.0192	480
12G	4.4	0.996	0.018	500	4.52^2	1.02	0.0197	790
12H	4.4	0.996	0.018	0	4.48^2	1.02	0.0190	500
12I	4.4	0.996	0.018	0	4.41^3	0.98	0.0185	480
SPC-1	4.4	0.996	0.018	0	4.50^2	1.02	0.0192	460
SPC-2	4.4	0.996	0.018	0	4.53^2	1.03	0.0195	500

1) ICP Job #: 98028   2) ICP Job #: 98046qw   3) ICP Job#: 98058

which the different powders were analyzed. The analysis technique has improved with time (going from 98028 to 98046qw to 98058). Within each analysis lot, the ICP values are very close indicating a high reproducibility in the powder synthesis procedure. The aluminum analysis shows that there is a background of ~500 ppm even when no Al is added. This background concentration is consistent with the amount of Al found as an impurity in the Zr n-butoxide lot used for powder synthesis. The ICP results also show that with respect to

composition, there is no difference between powders prepared by the batch or the continuous version of the Sandia Process.

Particle size distribution data were obtained on powders after the calcination step using a Coulter Model LS 230 particle size analyzer. Powder samples were ultrasonically dispersed (Heat Systems Model W375 sonic probe) for three minutes in filtered tap water using Darvan 821A as the dispersant . Figure 8 summarizes the results of these analyzes for powders 12A through 12F and the continuously prepared powders. The data in the figure
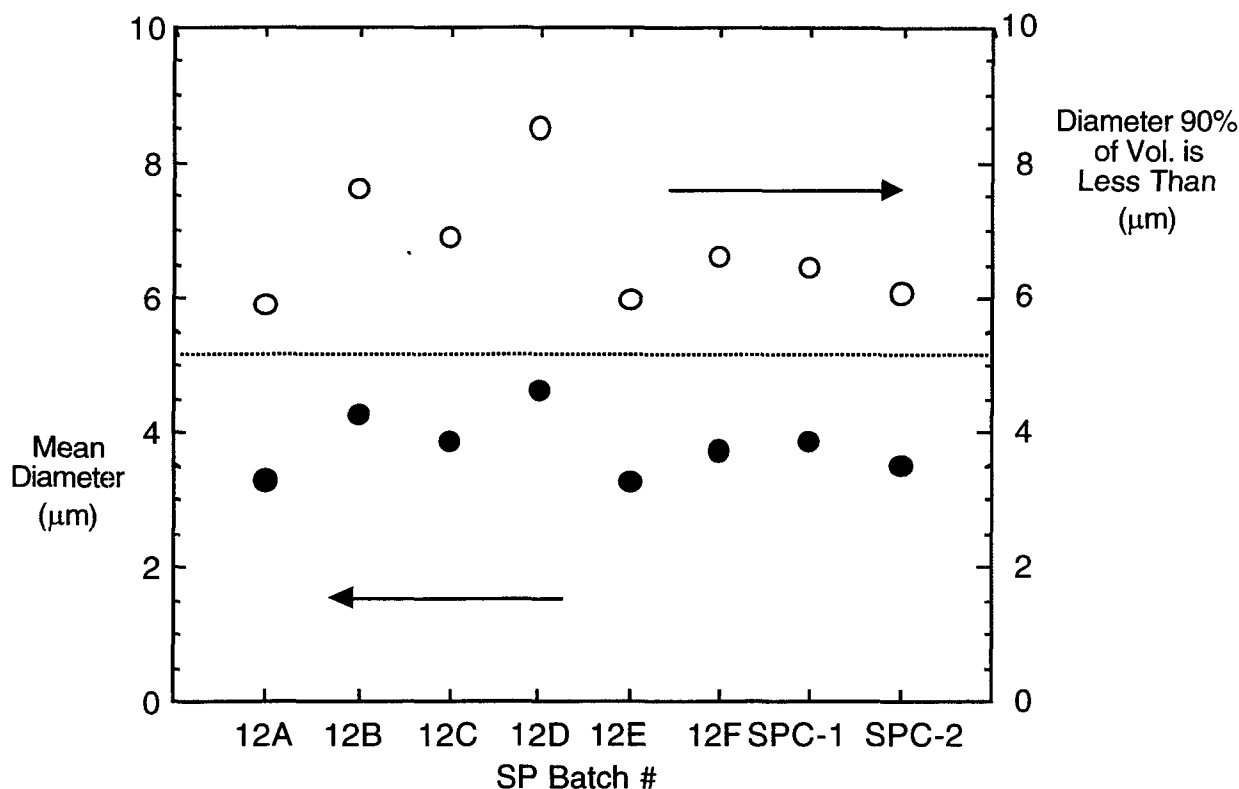
Figure 8.   Particle size data for a variety of SP powders obtained using the Coulter Model LS 230 particle size analyzer.

illustrates that the Sandia synthesis process is very reproducible with respect to powder paticle size. Powder surface areas are also highly reproducible as shown by the BET surface area data presented in Table 6. Also included in Table 6 are densification and sintering data for the powder lots that have been processed into ceramic form. An acrylic binder (HV4A) and 1.8 weight percent of the pore former avicel were added to the powders using a v-blender. The aggregated powders were uniaxially pressed at 2 ksi and isostatically pressed at 30 ksi. The pore former and binder were removed from the compacts during bisque firing at 750°C. The bisque fired samples were sintered at 1350°C for six hours using a triple crucible technique to prevent lead loss.

Table 6. Powder Surface Areas and Sintering Data for the SP12 Batch Powder Series and the SPC Continuously Precipitated Powder Series

Powder Batch #	Powder Surface Area (m^2/g)	Bisque Density (g/cm^3)	Fired Density (g/cm^3)	% Open Porosity
12A	1.30	4.49	7.37	0.3
12B	-	4.43	7.31	0.2
12E	1.29	4.44	7.43	0.1
12G	1.31	4.38	7.32	0.2
12H	1.10	4.41	7.43	0.2
SPC-1	1.20	(1)	(1)	(1)
SPC-2	1.32	4.47	7.46	0.1

(1) In process.

From Table 6, it is seen that the process is highly reproducible in going from the initial calcined powder to the final ceramic form. The target fired density for the neutron generator application is 7.2 to 7.5 g/cm^3 with very little open porosity. The data show that our sintered densities and open porosities are all on target for the application of interest. Finally, the data show that the continuously prepared powder (SPC-2), has fired properties similar to those of the batch processed material.

Electrical Characterization

The results of electrical characterization and explosive functional testing of the Sandia Process chem-prep PZT 95/5 material has shown that it can meet all of the neutron generator power supply requirements. In this section examples of typical ferroelectric hysteresis and depoling curves are given. Also, the most recent electrical and functional test data is summarized. Ceramic samples described in the last section were fabricated into voltage bar components and explosive functional test units (FTUs) by the Active Ceramics Team at Sandia. The Active Ceramics Team also did the electrical characterization, while the explosive testing was performed by the Organization 14302-2.

Figures 9 and 10 show a typical hysteresis loop and hydrostatic depoling curve, respectively, for the SP chem-prep material. The gradual charge release in the early stage of hydrostatic depoling curve is typical for samples with low open porosity (0.4 % for the example given in Figure 10). The within lot variability of the chem-prep material's electrical properties has been found to be very low. For example, the average value of the remnant polarization for the lot of material represented in Figures 9 and 10 (SP-9, Lot #9734, 10 samples tested), was 30.2 $\mu C/cm^2$ with a standard deviation of 0.1 $\mu C/cm^2$. The average hydrostatic depoling pressure (10 samples depoled) was 33.7 ksi with a standard deviation of 0.7 ksi. The low scatter in these values is again indicative of the high level of homogeneity built into the material through use of the solution chemistry approach.
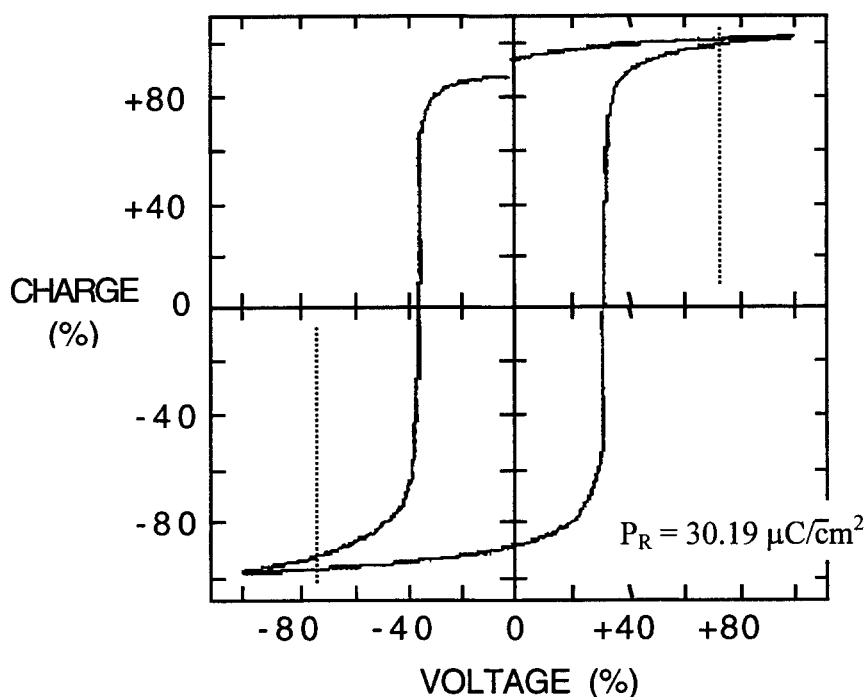
Figure 9.   Ferroelectric hysteresis loop of a voltage bar prepared from SP11 powder (FTU build lot # = 9734). This sample had a remnant polarization, P_R, of 30.19 $\mu C/cm^2$ (fired density of this lot was 7.38 g/cm^3 with 0.4% open porosity).
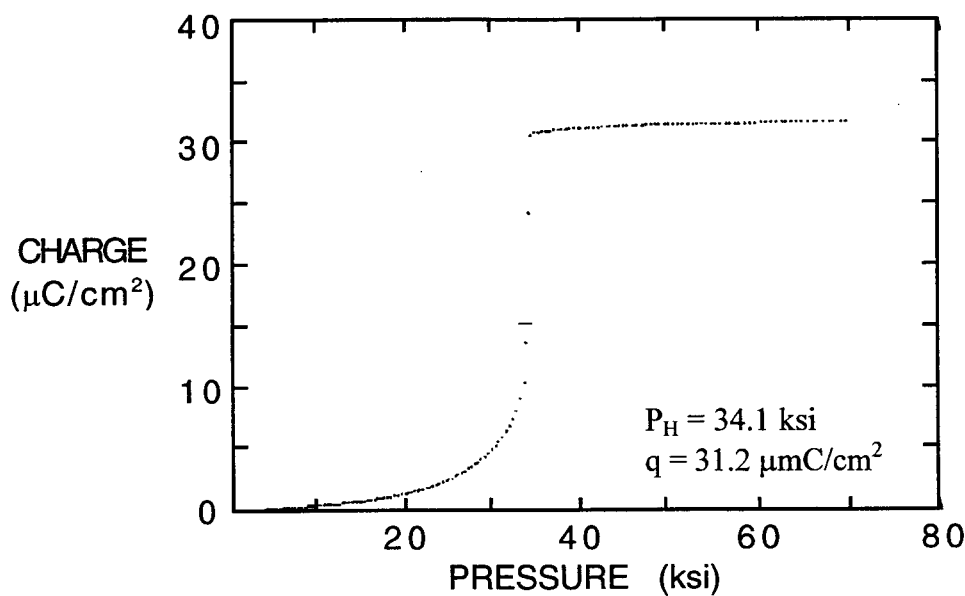
Figure 10.   Hydrostatic depoling curve of a voltage bar prepared from SP11 powder (FTU build lot # = 9734). This sample had a hydrostatic depoling pressure, P_H, of 34.1ksi with a charge release, q, of 31.2 $\mu C/cm^2$ (fired density of this lot was 7.38 g/cm^3 with 0.4% open porosity).

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The electrical properties and the results of explosive functional testing of the 12A series powders that have been processed are given in Table 7. These lots where batched to have the same ratios of Zr to Ti and Nb to Ti. It is these ratios of constituent metals that largely determines the pressure required to depole a PNZT 95/5 sample (there is approximately a 1 ksi increase in the pressure required in going from a Zr:Ti ratio of 95.7:4.3 to a ratio of 95.6:4.4). The fact that there is such a close grouping of the depoling pressures shown in the table is another indication of the high degree of control of powder stoichiometry achieved with the Sandia process. The combined average depoling pressure for the five lots is 35.0 ksi with a standard deviation of 0.5 ksi.

Table 7. Summary of Electrical Characterization Data and Explosive Functional Test Results for SP12 Series Material [1]

Powder Batch #	FTU Lot #	P_R[2] $(\mu C/cm^2)$	Depoling		UDS[5] (KV)	# Pass[6]/ # Tested
			P_H[3] (ksi)	q[4] $(\mu C/cm^2)$		
12A	9803	28.9 (0.3)	35.7 (0.7)	29.3 (0.4)	71.8 (4.1)	10/10
12B	9813	30.2 (0.1)	34.2 (0.4)	30.4 (0.3)	60.4 (4.6)	9/10
12E	9816	30.7 (0.2)	34.9 (0.2)	30.9 (0.1)	74.2 (7.8)	10/10
12G	9818	29.8 (0.1)	35.0 (0.1)	30.0 (0.1)	63.9 (17.1)	10/10
12H	9819	30.6 (0.1)	35.1 (0.1)	30.8 (0.1)	77.9 (8.3)	10/10

1) Values given are averages with numbers in parentheses the standard deviations.
2) Remnant polarization.
3) Hydrostatic depoling pressure.
4) Charge release on depoling.
5) Ultimate dielectric strength.
6) Number explosive functional test units that passed over the number of units tested.

The true test of the PNZT 95/5 chem-prep material with respect to its application in neutron generator power supplies is its performance during explosive functional testing. For each of the powder lots given in Table 7, 10 functional test units were fabricated and explosively tested. Of the 50 units tested for these lots there was only one failure. Although this work has only been taken through the developmental laboratory-scale stage, these results are very encouraging.

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Other Formulations

The Sandia Process readily lends itself to modifications that enable ceramic powders with varied stoichiometries to be prepared. Powders with several different compositions were prepared that are of interest to Sandia for a variety of applications, including high energy density capacitors, the Direct Fabrication Program, and slim loop ferroelectrics for firesets. In the five cases that will be described in further detail, the baseline synthetic process was followed, with minor modifications to the actual processing steps (some of these formulations were prepared prior to the optimization of the processing parameters), as well as the incorporation of different cations. In general, for the formulations other than PNZT, additional cations (Mg, Cu, Ba and Bi in these examples) were solubilized in the lead acetate solution, which when mixed with the alkoxides of Ti, Zr and/or Nb, formed the metal solution.

Lead Zirconate, (PZ)

A 75g batch of lead zirconate, PZ, was prepared with the composition of $Pb_{1.03}ZrO_3$. A Pb acetate solution (102.69g of a 0.00213 mol Pb/g solution) and a Zr n-butoxide/acetic acid solution (98.91g Zr n-butoxide, 0.204g Zr/g Zr n-butoxide, plus 12.77 g glacial acetic acid) were mixed for 37 minutes. This solution was pumped at 40 ml/minute into a solution of 69.48g of anhydrous oxalic acid dissolved in 397g of n-propanol at 49°C, with agitation supplied by a magnetic stir bar, manual stirring with a stir rod, as well as shear mixing. The slurry was stirred for 100 minutes, transferred to a medium frit glass filter funnel, and vacuum filtered. The wet filter cake was dried at 89°C for 44 hours. The dried powder was calcined at 775°C for 15.3 hours to form the desired perovskite $PbZrO_3$ phase.

Lead Niobate Zirconate Titanate (PNZT 52/48)

A 1.5kg batch of PNZT 52:48 was prepared with the composition of $Pb_{1.0473}Nb_{0.024}$ $(Zr_{0.52}Ti_{0.48})_{0.976}O_3$. For this batch, 1089.0g Zr n-butoxide (0.203g Zr/g Zr n-butoxide), 748.6g Ti n-butoxide (0.140g Ti/g Ti n-butoxide), and 50.8 g Nb n-butoxide (0.205g Nb/g Nb n-butoxide), were reacted with 281.91g glacial acetic acid for 5 minutes before being added to a Pb acetate solution containing 4.9154 moles Pb. This metals solution was mixed with an overhead stirrer for 30 minutes while under an N_2 purge. It was pumped into a 25 liter stirred vessel containing a solution of 1713.9g of anhydrous oxalic acid dissolved in 7018g n-propanol at 50°C over 16.5 minutes. The modes of agitation for the precipitation reaction were an overhead stirrer utilizing a 10 inch wide U-shaped paddle stirrer as well as a shear mixer. Upon completion of the metals solution addition, both the shear mixer and the external heat source were turned off. The slurry experienced an exothermic temperature increase of 4°C during stirring. After 90 minutes, the slurry was transferred to medium frit glass filter funnels, allowed to settle 11-15 minutes, vacuum filtered, and the resulting filter cake was dried at 88°C for 137 hours. The dried powder was calcined for 16 hours at ~400°C followed by 16 hours at ~770°C to form the desired PNZT 52/48 phase.

Lead Barium Zirconate Titanate/Bismuth (PBZTB)

An 80g batch of PBZTB was prepared with the composition of $(Pb_{0.71}Ba_{0.29})_{0.99}$ $(Zr_{0.707}Ti_{0.293})_{0.98}Bi_{0.02}O_3$. For this batch, 92.31g Zr n-butoxide (0.203g Zr/g Zr n-butoxide) and 28.34g Ti n-butoxide (0.140g Ti/g Ti n-butoxide) were reacted with 17.1g glacial acetic acid for 6 minutes before being added to a Pb-Ba-Bi acetate/acetic acid solution. The Pb-Ba-Bi solution was prepared by mixing 98.44g of Pb acetate solution (0.00208 mol Pb/g solution, with 86.1g of glacial acetic acid, 2.26 Bi acetate, and 21.35g of Ba acetate. The Pb-Ba-Bi-Zr-Ti solution was mixed for 4 minutes, and then poured quickly into a solution containing 106.3g oxalic acid (anhydrous) dissolved in 488g n-propanol with agitation provided by a stir bar as well as manual stirring with a spatula. The slurry was stirred for about 1.2 hours, transferred to a medium frit glass filter funnel and vacuum filtered. The wet filter cake was dried at 87°C for 90.5 hours. The dried powder was calcined at 400°C for 16 hours followed by 8 hours at 700°C.

Lead Magnesium Niobate Titanate/Cu (PMNTC)

A 25g batch of PMNTC was prepared with the composition $Pb_{1.03}Mg_{0.3147}Nb_{0.6293}Ti_{0.05}$ $Cu_{0.006}O_3$. For this batch, 36.10g of a lead acetate solution (0.002158 mol Pb/g solution) was mixed with 5.104g of Mg acetate ,0.091g of Cu acetate monohydrate, and 19.1g glacial acetic acid. The Ti-Nb solution was prepared by mixing 1.462g Ti n-butoxide (0.141g Ti/g Ti n-butoxide), and 23.90g Nb n-butoxide (0.204g Nb/g Nb n-butoxide), and 10.36g glacial acetic acid for 1.2 hours. A 32.14g aliquot of the Ti-Nb solution was added to the Pb-Cu-Mg solution and allowed to mix for 15 minutes. The Pb-Mg-Nb-Ti-Cu solution was rapidly poured into a warm solution containing 49.4g oxalic acid (dihydrate) dissolved in 96g n-propanol. The resulting slurry was stirred for 2 hours, transferred to a medium frit glass filter funnel and vacuum filtered. The wet filter cake was dried at 90°C for 89 hours. The dried powder was calcined at 500°C for 4 hours followed by 3 hours at 700°C. The percent recovery of components during precipitation was 99.1% for Nb and 99.6% for Ti.

Lead Magnesium Niobate/Lead Titanate (PMN/PT)

A 20g batch of PMN/PT was prepared with the composition $Pb_{1.06}Mg_{0.1637}$ $Nb_{0.3280}Ti_{0.5051}Cu_{0.0031}O_3$. For this batch, 29.06g of a lead acetate solution (0.002235 mol Pb/g solution) was mixed with 3.126g of Mg acetate, 0.039g of Cu acetate monohydrate, and 9.0g glacial acetic acid. The Ti-Nb solution was prepared by mixing 11.07g Ti n-butoxide (0.141g Ti/g Ti n-butoxide), and 9.63g Nb n-butoxide (0.204g Nb/g Nb n-butoxide), and 7.72g glacial acetic acid for 15 minutes. A 27.05g aliquot of the Ti-Nb solution was added to the Pb-Cu-Mg solution and allowed to mix for 20 minutes. The Pb-Mg-Nb-Ti-Cu solution was rapidly poured into a 50°C solution containing 31.1g oxalic acid (dihydrate) dissolved in 77g n-propanol. The resulting slurry was stirred for 1.5 hours, transferred to a medium frit glass filter funnel and vacuum filtered. The wet filter cake was dried at 50°C for 168 hours. The dried powder was calcined for 3 hours at 700°C. The percent recovery of components during precipitation was 99.99% for Pb, 99.95% for Mg, 99.99% Nb and 99.99% for Ti.

Summary

The main goal of this project at its inception was to develop a highly reliable and reproducible process for preparing PNZT 95/5 for neutron generator applications. With this objective in mind, we have developed a new nonaqueous synthesis route to lead-based ferroelectric materials. The process was designed such that: (1) waste generation is minimized(130 g PNZT/ liter of starting solutions); (2) the number of processing steps is minimized (easily filterable, no washing, no spray/freeze drying); (3) constituent metal cations are quantitatively removed from solution (>99.6% efficient) and (4) the process chemistry is versatile enough that it can be modified to produce a wide range of compositions. A patent for the process has been filed [14]. The process has been scaled to produce 1.6 kg of oxide powder in the lab in either a batch or a continuous fashion.

In keeping with the main objective of the project, most of our work was focused on the preparation of PNZT 95/5 powders. Characterization of powders from several 1.5 kg PNZT 95/5 batches showed the process to be highly reproducible with respect to powder properties, including composition, particle size distribution, surface area, and densification behavior. The ceramics prepared from these powders had very good electrical properties that also were very reproducible. When samples from these lots were explosively functionally tested, several lots of ten units passed the test with no failures. Because of these encouraging results with regard to process reproducibility and the powder being processable into material that meets neutron generator requirements, the Sandia Process is being strongly considered for scale-up to production levels.

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Appendix A: Calculation of Effective Formula Weights

The following details the calculations of the amounts of the n-butoxides of Zr, Ti, and Nb to use based on elemental analyses:

<u>Zr Calculations</u>

The Zr n-butoxide contains some Ti and Hf owing to the chemical similarity of the Group 4B metal ions. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) is used to determine the concentration of Ti in the Zr source. There are 310 ppm Ti in the Zr n-butoxide. This is converted to grams of TiO_2:

$$\frac{0.031 \, g \, Ti}{47.90 \, g \, Ti / mol} \; x \; \frac{1 \, mol \, TiO_2}{1 \, mol \, Ti} x \; \frac{79.90 \, TiO_2}{mol \, TiO_2} = 0.0517 \, g \, TiO_2$$

From ICP-AES the concentration of Hf in the Zr n-butoxide is 0.483 weight percent. This is converted to grams of HfO_2:

$$\frac{0.483 \, g \, Hf}{178.49 \, g \, Hf / mol \, Hf} \; x \; \frac{1 \, mol \, HfO_2}{1 \, mol \, Hf} x \; \frac{210.49 \, g \, HfO_2}{mol \, HfO_2} = 0.5696 \, g HfO_2$$

From ICP-AES the butoxide is 19.68 weight percent Zr, which is converted to grams ZrO_2:

$$\frac{19.683 \, g \, Zr}{91.22 \, g \, Zr / mol Zr} \; x \; \frac{1 \, mol \, ZrO_2}{1 \, mol \, Zr} x \; \frac{123.2 \, g \, ZrO_2}{mol \, ZrO_2} = 26.584 \, g \, ZrO_2$$

The weight percent oxides from ICP-AES is then calculated by summing the weights of the oxides:

$$0.0517 \, g \, TiO_2 + 0.5696 \, HfO_2 + 26.584 \, ZrO_2 = 27.205 \, g \, oxides$$

This is compared to the weight percent determined by conventional gravimetric analysis (performed by heating the hydolyzed butoxides to 1000°C for 2 hours) of 27.897 g. These results are used to determine a gravimetric factor (GF):

$$GF = \frac{27.897 \, g \, oxides}{27.205 \, g \, oxides} = 1.0254$$

The gravimetric factor multiplied by the number of grams of the oxides determined from ICP results in the number of grams of oxides per 100 g of Zr n-butoxide. (Essentially the

trace analyses are used to determine the concentration of Ti and Hf in the butoxide, and the conventional gravimetric analysis is used to determine the overall concentration of oxides in the butoxide):

$$0.0517 \text{ g } TiO_2 \text{ x } 1.0254 \ = \ \frac{0.05301 \text{ g } TiO_2}{100 \text{ g } Zr \text{ n - butoxide}}$$

$$0.5696 \text{ g } HfO_2 \text{ x } 1.0254 \ = \ \frac{0.5841 \text{ g } HfO_2}{100 \text{ g } Zr \text{ n - butoxide}}$$

$$26.584 \text{ g } ZrO_2 \text{ x } 1.0254 \ = \ \frac{27.259 \text{ g } ZrO_2}{100 \text{ g } Zr \text{ - butoxide}}$$

Now, the effective moles of Hf + Zr per 100 g Zr n-butoxide is calculated

$$Hf = \frac{0.5841 \text{ g } HfO_2 / 100 \text{ g } n \text{ - butoxide}}{210.49 \text{ g } HfO_2 / \text{mol } HfO_2} = \frac{0.00277 \text{ mol } HfO_2}{100 \text{ g } n \text{ - butoxide}}$$

$$Zr = \frac{27.259 \text{ g } ZrO_2 / 100 \text{ g } n \text{ - butoxide}}{123.22 \text{ g } ZrO_2 / \text{mol } ZrO_2} = \frac{0.2212 \text{ mol } ZrO_2}{100 \text{ g } n \text{ - butoxide}}$$

These two are summed to give:

$$"Hf + Zr" = \frac{0.22399 \text{ mol } Hf + Zr}{100 \text{ g } n \text{ - butoxide}}$$

The amount of Zr n-butoxide to use per 100 g PNZT can then be calculated from:

$$\frac{0.2920 \text{ mol } PNZT / 100 \text{ g } PNZT \text{ * } 0.9329 \text{ mol } Zr / 100 \text{ g } PNZT}{0.00224 \text{ mol } "Hf + Zr"/g \text{ } Zr \text{ n - butoxide}} = \frac{121.610 \text{ g } Zr \text{ n - butoxide}}{100 \text{ g } PNZT}$$

To account for the Ti in the Zr n-butoxide:

$$\frac{0.00053 \text{ g } TiO_2/1g \text{ } Zr \text{ n-butoxide } \text{ * } 121.610 \text{ g } Zr \text{ n-butoxide}}{79.90 \text{ g } TiO_2 / \text{mol } TiO_2} = \frac{0.00081 \text{ mol } TiO_2}{1 \text{ g } Zr \text{ n-butoxide}}$$

The number of moles of Ti n-butoxide needed per 100 g PNZT is thus:

$$\frac{0.2920 \ mol \ PNZT}{100 \ g \ PNZT} \ x \ \frac{0.0491 \ mol \ Ti}{mol \ PNZT} = \frac{0.01434 \ mol \ Ti}{100 \ g \ PNZT}$$

So the amount of Ti contributed by the Zr n-butoxide is subtracted from the total amount of Ti required, resulting in the number of moles of Ti n-butoxide needed per 100 g PNZT:

$$\frac{0.01434 \ mol \ Ti}{100 \ g \ PNZT} - \frac{0.00081 \ mol \ Ti}{121.61 \ g \ Zr \ n-butoxide} = \frac{0.01353 \ mol \ Ti}{100 \ g \ PNZT}$$

Thus the number of grams of Ti n-butoxide added per 100 g PNZT is:

$$\frac{0.01353 \ mol \ TiO_2 \ * \ 79.9 \ g \ TiO_2 \ / \ mol \ TiO_2}{0.2345 \ g \ TiO_2 \ / \ g \ Ti \ n-butoxide} = \frac{4.609 \ g \ Ti \ n-butoxide}{100 \ g \ PNZT}$$

The amount of Nb n-butoxide is calculated from the gravimetric assay (29.12 wt% Nb_2O_5 Inorgtech Lot 3096):

$$\frac{0.018 \ mol \ Nb}{mol \ PNZT} \ x \ \frac{0.2920 \ mol \ PNZT}{100 \ g \ PNZT} = \frac{0.00526 \ mol \ Nb}{100 \ g \ PNZT}$$

The amount of Nb n-butoxide per 100 g PNZT is then calculated from:

$$\frac{0.00526 \ mol \ Nb}{100 \ g \ PNZT} \ x \ \frac{1 \ mol \ Nb_2O_5}{2 \ mol \ Nb} \ x \ \frac{265.812 \ g \ Nb_2O_5}{mol \ Nb_2O_5} \ x \ \frac{1 \ g \ Nb \ n-butoxide}{0.2912 \ g \ Nb_2O_5}$$

$$= \frac{2.399 \ g \ Nb \ n-butoxide}{100 \ g \ PNZT}$$

The number of moles of Pb acetate for 0% excess is calculated from:

$$\frac{0.9910 \ mol \ Pb}{mol \ PNZT} \ x \ \frac{0.2920 \ mol \ PNZT}{100 \ g \ PNZT} = 0.2894 \ mol \ Pb$$

The moles of Pb is then divided by the concentration of the Pb acetate concentration to get the number of grams of solution needed:

$$\frac{0.2894 \; mol \; Pb}{100 \; g \; PNZT} \; x \; \frac{1 \; g \; Pb \; acetate}{0.00225 \; mol \; Pb} = \frac{128.6222 \; g \; Pb \; aceate}{100 \; g \; PNZT}$$

Note the amount of Pb acetate varies from run to run depending on excess desired and its concentration.

Appendix B: Analytical Data

Summary of Elemental Analyses

Inductively coupled plasma (ICP) analyses are performed on filtrate and calcined powder. During the precipitation step of the process, aliquots of the filtrate are taken to monitor percent recovery of the metals for a particular batch. The final calcined (900°C) powder is analyzed for powder composition by the Analytical Chemistry Laboratory (Department 1824).

The final method developed for analysis of the filtrate for percent recovery involves air drying at ~88°C three aliquots of the filtrate in glass vials. The dried residue is decomposed at ~425°C for 4 hours in air and dissolved in a mixture containing 1 ml concentrated HNO_3 and 3 ml concentrated HCl. The mixture is allowed to digest until the residue is dissolved (~2 days). It is diluted to 25 ml and analyzed on a Perkin Elmer Plasma 400 ICP for Pb, Zr, Ti and Nb.

The percent recovery results for the Plackett Burman matrix (see Table 1b for batch description) is shown in Table B-1. For the matrix study, the general trend is that Pb and Zr are quantitatively precipitated (>99.99% recovery), Nb is recovered at the 99.86 to 99.98% level, and Ti is recovered at the 99.27 to 99.99 % level. The Ti recovery can be as low as 99.27% for batches made with dilute oxalic acid (10 wt%), a large excess of oxalic acid (OA:metal = 4.0), and hydrated oxalic acid (batches SP3I,J).

Table B-1. Percent Metals Precipitated for the Plackett Burman Series of Runs (SP3)

Sample ID	percent recovery, Zr	percent recovery, Nb	percent recovery, Ti	percent recovery, Pb
SP3B-1	99.999	99.988	99.993	99.999
SP3C-1	99.998	99.944	99.936	100
SP3D-1	99.990	99.967	99.963	100
SP3E-1	99.995	99.868	99.867	100
SP3H-1	99.994	99.945	99.958	99.999
SP3I-1	100	99.891	99.602	99.999
SP3J-1	99.996	99.875	99.279	99.999
SP3K-1	99.999	99.977	99.98	99.998
SP3L-1	99.995	99.954	99.925	100
SP3O-1	99.999	99.988	99.967	100

(SP3O-1 was not part of the matrix. The batch parameters were as for SP3E-1, but the reaction was done at room temperature. Batches SP3A, F, G and N were unfilterable; batch SP3M was not analyzed.

Shown below (Table B-2) are more percent recovery (metals) results for batches prepared with various parameters and processing changes. SP4A is a 400g batch using preliminary optimized parameters from the matrix. Batches 5A & B, the SP6 series, and 7A continue with similar parameters as SP4A, but processing parameters involve scaling-up and slight stoichiometry changes. Beginning with SP7B the use of Tekmar shear mixer was incorporated into the synthesis process. No major changes are seen in percent recovery of the metals through the series of batches beginning with SP7B even though experimental processing parameters varied. Some of these variations include: (1) the use of new shear mixer parts beginning first with SP11C and then again in SP13D; (2) the increase in the setting of the shear mixer speed to 75 from 50 (beginning with SP12E); (3) a decrease in the oxalic acid solution temperature from 50°C to 35°C (beginning with SP11C); (4) the incorporation of an in-line 5 μm filter in the metals solution stream (beginning with SP12H); (5) positioning the metals solution inlet tube near the inlet ports of the shear mixer head, first with SP11E, and then becoming standard in batches made on/after 11-20-97.

Table B-2. Percent Metal Precipitated for a Variety of SP Batches

Sample ID	percent recovery, Zr	percent recovery, Nb	percent recovery, Ti	percent recovery, Pb	date prepared
SP4A-4	99.999	99.987	99.907	99.999	12/10/96
SP5A-10	100	99.979	99.941	100	12/17/97
SP5B-14	99.998	99.959	99.885	99.998	1/27/97
SP6A-15	99.999	99.94	99.828	99.999	1/30/97
SP6B-15	100	99.905	99.802	99.999	2/3/97
SP6C-15	99.999	99.943	99.875	99.999	2/6/97
SP7A-15	99.999	99.95	99.836	99.999	2/10/97
SP7B-15	99.998	99.561	99.641	99.998	3/4/97
SP7C-15	99.998	99.954	99.813	99.998	2/27/97
SP7D-15	99.998	99.921	99.815	99.997	3/10/97
SP7E-15	99.999	100	99.843	99.999	3/7/97
SP7F-15	99.999	99.889	99.857	99.999	4/3/97
SP8A-3	99.988	99.184	99.697	99.992	2/19/97
SP8B-13	99.998	99.803	99.812	99.999	2/24/97
SP9A-15	99.999	99.891	99.887	100	6/3/97
SP9B-15	99.999	99.842	99.85	99.999	6/5/97
SP9C-15	99.999	99.746	99.81	99.999	6/12/97
SP9D-15	99.999	99.739	99.798	99.999.	6/17/97
SP11A-15	99.999	99.753	99.79	100	8/13/97
SP11B-15	99.998	99.846	99.828	99.999	8/20/97
SP11C-15	100	99.974	99.791	100	10/1/97
SP11D-15	100	99.953	99.727	100	10/29/97
SP11E-15	100	99.977	99.836	100	11/4/97
SP11F-15	100	99.981	99.833	100	11/6/97
SP11G-15	100	99.941	99.873	100	11/13/97
SP11H-15	100	99.936	99.874	100	11/18/97
SP11I-15	100	99.961	99.764	100	12/10/97
SP12D-15	100	99.941	99.738	100	3/4/98
SP12F-15	100	99.962	99.781	100	3/18/98
SP12H-16	100	99.905	99.714	100	4/23/98
SP12I-16	100	99.887	99.687	100	5/20/98
SP13A-16	100	99.898	99.694	100	5/7/98
SP13B-16	99.999	99.825	99.677	99.999	6/2/98
SP13C-16	99.999	99.812	99.672	99.999	7/15/98
SP13D-16	99.999	99.82	99.631	100	7/30/98
SP14B-16	99.999	99.849	99.671	99.999	7/1/98

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Appendix C: Sample PNZT Logsheet

Batch: **Notebook #s:**   **Date:**

Moles PNZT: **Excess Pb:**   **Grams PNZT:**

                             Pb acetate NB#:   **Grams Prec.:**

Target Stoichiometry: R_H:

Reagents

Reagent	Calc. wt.	Actual wt.	Time	Lot #	Comments
$Zr(OBu^n)_4$					
$Ti(OBu^n)_4$					
$Nb(OBu^n)_5$					
acetic acid					
Pb acetate					
oxalic acid					
n-propanol					

Synthesis Parameters

Parameter	Symbol	Target	Actual	Comments
alk. mix time	t_{alk}			
metal soln mix time	t_{metal}			
precip. mixing time	t_{precip}			
time to add metal soln.	$t_{metal\ addn}$			
temp. of oxalic acid soln.	T_{OA}			
precipitate stirring speed	S_{precip}			
external heat	Heat			

Chemical Information
AA:Alk -
H_2O:PNZT -
OA:metal -
[OA] -

Observations
Max ΔT -
Min/Max Torque -

Calculations:

OA: effective F.W. OA * OA:metal * moles PNZT =

n-propanol:
actual g OA = (94.07 g/mol)/effective F.W. OA * grams OA =

mL n-propanol = (actual g OA – 0.177(g OA + g H_2O))/
                        (0.177 * 0.802 g/mL) =

Appendix D: Sample Lead Acetate Preparation Sheet

Notebook #:   **Date:**
Batch:

Target grams PNZT: **PbO source:**

Excess Acetic Acid: **Excess Pb:**   **Transfer Factor:**

<u>Calculations</u>
Moles PNZT: (target grams PNZT/342.448 g/mol) =

Moles PbO for batch = $(0.991 + (0.01*\text{Excess Pb}))$ * (moles PNZT) =

Total Moles PbO = Moles PbO for batch * (transfer factor) =

Total Grams PbO = (total moles PbO) * 223.19 g/mole =

Grams acetic acid = (total moles PbO) * (excess AA) * 4.0 * 60.05 g/mol =

Milliliters acac = ((moles PbO) * 0.01 * 100.12 g/mol) / 0.975 g/cc =

<u>Tare Weights</u>
boat #1 -
boat #2 -
___L kettle -
lid -
teflon stirrer -
stopper ___ -
stopper ___ -
N_2 inlet -
AA beaker -

Final Concentration = (total moles PbO/g solution) =
Color/Clarity -

Wt. solution needed for batch: (moles PbO for batch/final concentration) =

Distribution:

<u>Internal Distribution Only:</u>

1	MS9018	Central Technical Files, 8940-2
2	0899	Technical Library, 4916
1	0619	Review & Approval Desk, 12690 For DOE/OST I
1	MS0188	LDRD Office, 4001
1	MS0343	W. B. Chambers, 1822
1	MS0367	S. J. Glass, 1833
1	MS0515	J. D. Keck, 1561
1	MS0521	T. W. Scofield, 1567
1	MS0959	S. J. Lockwood, 1492
1	0959	T. V. Montoya, 1492
1	0959	R. H. Moore, 1492
1	0959	P. Yang, 1492
1	0959	G. M. Goy, 1492
1	MS1349	K. G. Ewsuk, 1846
1	1349	W. F. Hammetter, 1846
1	1349	J. Cesarano, 1831
5	MS1405	J. A. Voigt, 1846
3	1405	D. L. Sipola, 1846
1	MS1411	D. B. Dimos, 1831